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VAPOR PRESSURES OF THE COMMON METALLIC CHLORIDES AND A STATIC METHOD FOR HIGH TEMPERATURES

BY
C. G. MAIER

This paper represents work done under a cooperative agreement between the Bureau of Mines, Department of the Interior and the Department of Metallurgical Research of the University of Utah

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CONTENTS

	Page
Introduction	1
Need for further data	1
Advantages of the present method	2
Acknowledgments	3
Determination of vapor pressures	3
Apparatus	3
Container, trap, and adjuncts	4
Manometer and adjuncts	6
Pressure regulation	6
Furnace and temperature regulation	7
Other accessory apparatus	10
Procedure	10
General preparation of materials	10
Handling a container before a determination	11
Protection of mercury in the trap	12
Determination	12
Method of calculation	13
Temperature correction	13
Note	14
Pressure calculation	14
Calculation from pressure and temperature readings	14
Experimental results	16
Group I. Monovalent metal chlorides	16
Lithium chloride	16
Preparation	16
Notes on determination	18
Sodium chloride	18
Cuprous chloride	18
Preparation	18
Notes on determination	19
Silver chloride	20
Preparation	20
Notes on determination	20
Sodium-silver chloride	22
Preparation	22
Notes on determination	22
Group II. Divalent metal chlorides	24
Zinc chloride	24
Preparation	24
Notes on determination	24
Cadmium chloride	25
Preparation	25
Notes on determination	25
Barium chloride	25
Preparation	26
Notes on determination	26
Calcium chloride	27
Preparation	27
Notes on determination	27

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Determination of vapor pressures—Continued
Experimental results—Continued
Group II. Divalent metal chlorides—Continued Page
Magnesium chloride 27
Preparation 28
Notes on determination 28
Lead chloride 28
Preparation 28
Notes on determination 28
Manganous chloride 30
Preparation 30
Notes on determination 30
Ferrous chloride 30
Preparation 31
Notes on determination 31
Nickel chloride 31
Preparation 31
Notes on determination 32
Cobalt chloride 33
Preparation 33
Notes on determination 34
Cupric chloride 34
Preparation 34
Notes on determination 36
Stannous chloride 36
Preparation 36
Notes on determination 36
Group III. Trivalent metal chlorides 38
Aluminum chloride 38
Preparation 38
Notes on determination 40
Ferric chloride 40
Preparation 40
Notes on determination 42
Arsenic chloride 42
Preparation 42
Notes on determination 42
Antimony trichloride 44
Preparation 45
Notes on determination 45
Bismuth trichloride 45
Preparation 45
Notes on determination 46
Calculated and derived results 46
Tables of vapor pressures 46
Values of heat of vaporization 46
Accuracy of results 50
Summary 51
Determination of dissociation pressures 52
Publications on the chloride volatilization of ores 54

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TABLES

		Page
TABLE 1.	Data on vapor pressures of lithium chloride (LiCl) at various temperatures	16
2.	Data on vapor pressures of sodium chloride (NaCl) at various temperatures	18
3.	Data on vapor pressures of cuprous chloride (Cu_2Cl_2) at various temperatures	19
4.	Data on vapor pressures of cuprous chloride (Cu_2Cl_2; duplicate) at various temperatures	20
5.	Data on vapor pressures of silver chloride (AgCl) at various temperatures	22
6.	Data on vapor pressures of sodium-silver chloride ($NaAgCl_2$) at various temperatures	22
7.	Data on vapor pressures of zinc chloride ($ZnCl_2$) at various temperatures	24
8.	Data on vapor pressures of cadmium chloride ($CdCl_2$) at various temperatures	25
9.	Data on vapor pressures of barium chloride ($BaCl_2$) at various temperatures	26
10.	Data on vapor pressures of magnesium chloride ($MgCl_2$) at various temperatures	27
11.	Data on vapor pressures of lead chloride ($PbCl_2$) at various temperatures	28
12.	Data on vapor pressures of manganous chloride ($MnCl_2$) at various temperatures	30
13.	Data on vapor pressures of ferrous chloride ($FeCl_2$) at various temperatures	31
14.	Data on vapor pressures of first sample of nickel chloride ($NiCl_2$) at various temperatures	32
15.	Data on vapor pressures of second sample of nickel chloride ($NiCl_2$) at various temperatures	32
16.	Data on vapor pressures of cobalt chloride ($CoCl_2$) at various temperatures	33
17.	Data on vapor pressures of cupric chloride ($CuCl_2$) at various temperatures	34
18.	Data on vapor pressures of stannous chloride ($SnCl_2$) at various temperatures	38
19.	Data on vapor pressures of aluminum chloride ($AlCl_2$) at various temperatures	40
20.	Data on vapor pressures of ferric chloride ($FeCl_3$) at various temperatures	40
21.	Data on vapor pressures of arsenic trichloride ($AsCl_3$) at various temperatures	42
22.	Data on vapor pressures of antimony trichloride ($SbCl_3$) at various temperatures	44

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Page

TABLE 23. Data on vapor pressures of bismuth trichloride ($BiCl_3$) at various temperatures 45
24. Vapor pressures and heats of vaporization of alkali chlorides. 46
25. Vapor pressures and heats of vaporization of heavy-metal monovalent chlorides 47
26. Vapor pressures and heats of vaporization of divalent chlorides, second periodic group 47
27. Vapor pressures and heats of vaporization of divalent chlorides, iron group, and manganese 47
28. Vapor pressures and heats of vaporization of divalent chlorides, remaining groups 48
29. Vapor pressures and heats of vaporization of trivalent chlorides. 49
30. Comparison of boiling points 50
31. Normal boiling points, arranged with decreasing temperatures 51

ILLUSTRATIONS

Page

FIGURE 1. Forms of containers, traps, and capsules 5
2. Containers in position previous to experiment 8
3. Diagrammatic set-up of apparatus 9
4. Logarithmic plot of vapor pressures of chlorides of the alkali metals (lithium, sodium, and potassium), silver, and cuprous copper 17
5. Logarithmic plot of vapor pressures of chlorides of magnesium, sodium silver, cadmium, and ferrous iron 21
6. Logarithmic plot of vapor pressures of zinc chloride 23
7. Logarithmic plot of vapor pressures of barium chloride 26
8. Logarithmic plot of vapor pressures of chlorides of lead, nickel, and cobalt 29
9. Logarithmic plot of vapor pressure of bismuth, mercurous, and cupric chloride 35
10. Logarithmic plot of vapor pressures of stannous chloride 37
11. Logarithmic plot of vapor pressures of chlorides of aluminum and antimony 39
12. Logarithmic plot of vapor pressure of bismuth, ferric, mercuric, and auric chlorides 41
13. Logarithmic plot of vapor pressures of arsenic trichloride 43
14. Apparatus for determining equilibrium pressure of dissociable chlorides 52

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THE VAPOR PRESSURES OF THE COMMON METALLIC CHLORIDES AND A STATIC METHOD FOR MEASUREMENT AT HIGH TEMPERATURES

By C. G. Maier

INTRODUCTION

The work described in this pamphlet was undertaken primarily to furnish technical data on the vapor pressures and heats of vaporization of the metallic chlorides at high temperatures. Persons interested in such figures do not need to be reminded of the inadequacy of the data found in the usual handbooks. In order to cover the field of the metallic chlorides of possible technical importance, this work was necessarily hurried through a series of measurements rich in interesting side issues.

Care was taken to eliminate as much as possible the more obvious sources of minor inaccuracy, but it can not be hoped that the results given could be all that are desirable as scientific data. For average technical purposes they are thought to be adequate. For a few chlorides, chiefly for those of copper, barium, and calcium, and perhaps a few others as noted, the results seem enough better than previous data to be corrective.

NEED FOR FURTHER DATA

In the past, study of the fundamentals of certain important metallurgical processes dealing with chlorides at high temperatures has been difficult, especially the chloridizing roast and chloride volatilization. One important reason for the difficulty has been the almost complete lack of vapor-pressure and thermal data that were technically usable. Such data are not only necessary to understand losses or vaporization of metals as chlorides, but they are essential to deal quantitatively with the chemical reactions that occur in the processes mentioned above. Many of the reactions taking place seem primarily to be vapor-phase reactions, whose study is only possible in the light of definite knowledge concerning the relative tendencies of the various chlorides to vaporize.

The Bureau of Mines, in its previous study of the processes mentioned, kept this need in mind, and a start toward furnishing data was

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made by Eastman and Duschak.[1] The dynamic method used by these authors, although satisfactory, was necessarily somewhat slow and laborious when many substances were to be measured, especially as each point of a vapor-pressure curve had to be determined by a separate experiment at a carefully controlled temperature. Moreover, for technical purposes a direct measurement of the actual pressure of vapor, involving no assumptions relative to the molecular weight of the vapor or its behavior according to the gas law, seemed preferable. A static method will in general fulfill these conditions and permit greater certainty that equilibrium between vapor and solid or liquid salt has been attained.

ADVANTAGES OF THE PRESENT METHOD

In view of these considerations, a method which has been used for the determinations described below was developed at the Salt Lake laboratories of the University of Utah and the bureau. By this method many points of a vapor-pressure curve could be found during the course of a single satisfactory experiment. Although perhaps the method is intrinsically less accurate for very low values of vapor pressure than the inert-gas saturation or the boiling-point methods, it has advantages, other than those mentioned in the preceding paragraph, of being usable well above the normal boiling point of materials when that temperature is obtainable with the apparatus used, and of working well either for vaporization or sublimation.

Practical temperature limits depend rather on the material chosen for the container than on the method used, and in this sense the method used in these experiments is probably the equivalent of any method usable at high temperatures. The static method used, however, is decidedly superior to any dynamic method in the relative ease with which determinations can be made on those chlorides having appreciable dissociation pressures at the temperatures under investigation. This phase is treated in some detail on pages 12 and 13.

To the technical reader interested in processes involving chlorides at high temperatures, the numerical results of this work may seem of more import than the method. A more complete description of the method used has been given than might seem advisable under other circumstances, but after the necessary apparatus is once assembled, determinations may be made more quickly and easily, according to requirements of the average technical laboratory, than by possibly more scientific methods. No especial originality is claimed for the method other than the adaptation of the means at hand.

[1] Eastman, E. D., and Duschak, L. H., The vapor pressure of lead chloride: Tech. Paper 225, Bureau of Mines, 1919, 16 pp.

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A critical comparison of vapor-pressure methods is not possible in this paper, but when determinations were made on chlorides for which data were available, the latter are given in some of the later tables. The results of some other investigators are included in the tables when the authors had made no actual determination for the chloride specified. The aim was to assemble as complete data as possible for the common metallic chlorides.

ACKNOWLEDGMENTS

The experimental work was undertaken under cooperative agreement between the department of metallurgical research of the University of Utah and the Intermountain station of the United States Bureau of Mines at Salt Lake City, largely during a period when the writer was assistant director of the university department. Thanks are extended to all who have aided in the work, especially to C. E. Baumgarten, metallurgical research fellow of the department, 1922–23, who was of much aid in the laboratory work and made the determinations of the chlorides of lead, lithium, cobalt, manganese, and bismuth.

DETERMINATION OF VAPOR PRESSURES

The principle of operation depended on the fact that after a container had been evacuated to a few centimeters absolute pressure, which was manually kept at constant volume by regulating the external pressure in the trap, any residual inert gas (N_2) obeyed the gas law as long as any material in the container had no appreciable vapor tension. When the temperature of the container slowly increased and actual vapor was being formed in the cylinder, the actual pressure of this vapor was determinable by comparing the actual pressure externally required to maintain constant volume with that calculated from the gas law for the residual inert gas. Corrections and fuller details of calculation are given on pages 13 to 15.

APPARATUS

The essential parts of the apparatus used in these experiments were: 1, A cylindrical container capable of being uniformly heated by insertion in the middle of an electric tube-furnace, and connected with outside accessory apparatus by means of a capillary of negligible volume as compared to the total volume; 2, a trap placed at the external end of the capillary mentioned to maintain the contents of the container at constant volume; 3, a manometer system connected with the outside of the trap, and capable of registering pressures from 0.5 cm. absolute to several atmospheres total; 4, a system of pressure and vacuum tanks, with suitable regulating valves and

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pumps, serving to control the pressure on the manometer side of the trap to within 0.2 mm. or closer.

CONTAINER, TRAP, AND ADJUNCTS

Various forms of container and trap were used, which differed only in minor details of method of filling, evacuating, and connection of the trap, etc. Figure 1, *A* to *D*, shows their general characteristics. For temperatures up to 650° C., heavy-walled pyrex tubing was found satisfactory for the container cylinder. For higher temperatures up to the maximum attainable in these experiments, 1,350° C., clear fused silica was used. Some of the earliest experiments were performed with ordinary vitreosil tubing, but this material often developed pinhole openings at the higher temperatures, and was almost impossible to keep gas-tight at high pressure. The clear silica glass, although quite expensive, is much easier to handle in blowing, and the maximum temperature at which it is usable for this purpose depends on the fact that it begins to have an appreciable vapor pressure of its own rather than on mechanical failure.

Figure 1, *A*, shows the original form, with dimensions, of the container and trap used for temperatures below 600° C. The material to be measured was first dehydrated with fusion and distillation when possible, collected in a small glass or silica boat, and inserted into the apparatus at *c*. One or two droplets of mercury were put into the trap *f*, and the rear end of the container drawn down preparatory to sealing off as at *a*–*a*. Dry gas was passed slowly through the apparatus, entering at N_2 and bubbling through *f*. The container was usually heated during this operation. After final dehydration and filling with dry nitrogen was complete, the material was cooled in a slow stream of nitrogen, the trap *f* then being filled to the proper level with carefully dried and purified mercury, and the whole sealed off at *a*–*a*.

The form shown in Figure 1, *A*, was not entirely satisfactory for hygroscopic chlorides, or those appreciably volatile at the dehydrating temperature. To reverse the direction of nitrogen flow, to prevent clogging the capillary with condensed vapors, and to do the filling as nearly as possible out of contact with air were desirable. Figure 1, *B*, shows a satisfactory form of container which met these requirements. The anhydrous chloride was previously prepared in the sealed capsule *c*. At *g* a capillary outlet, *i*, with a heavy-walled rubber connector tube and a pinchcock, *j*, was sealed into the bend of the capillary. The joint between rubber and capillary was sealed with de Khotinsky cement *l*. Dry nitrogen was passed in at N, and out at *h*. When the tube was dried by gently heating during the preliminary passage of nitrogen, the end of the capsule at *c* was broken, and the contents of *c* permitted to run into the container by

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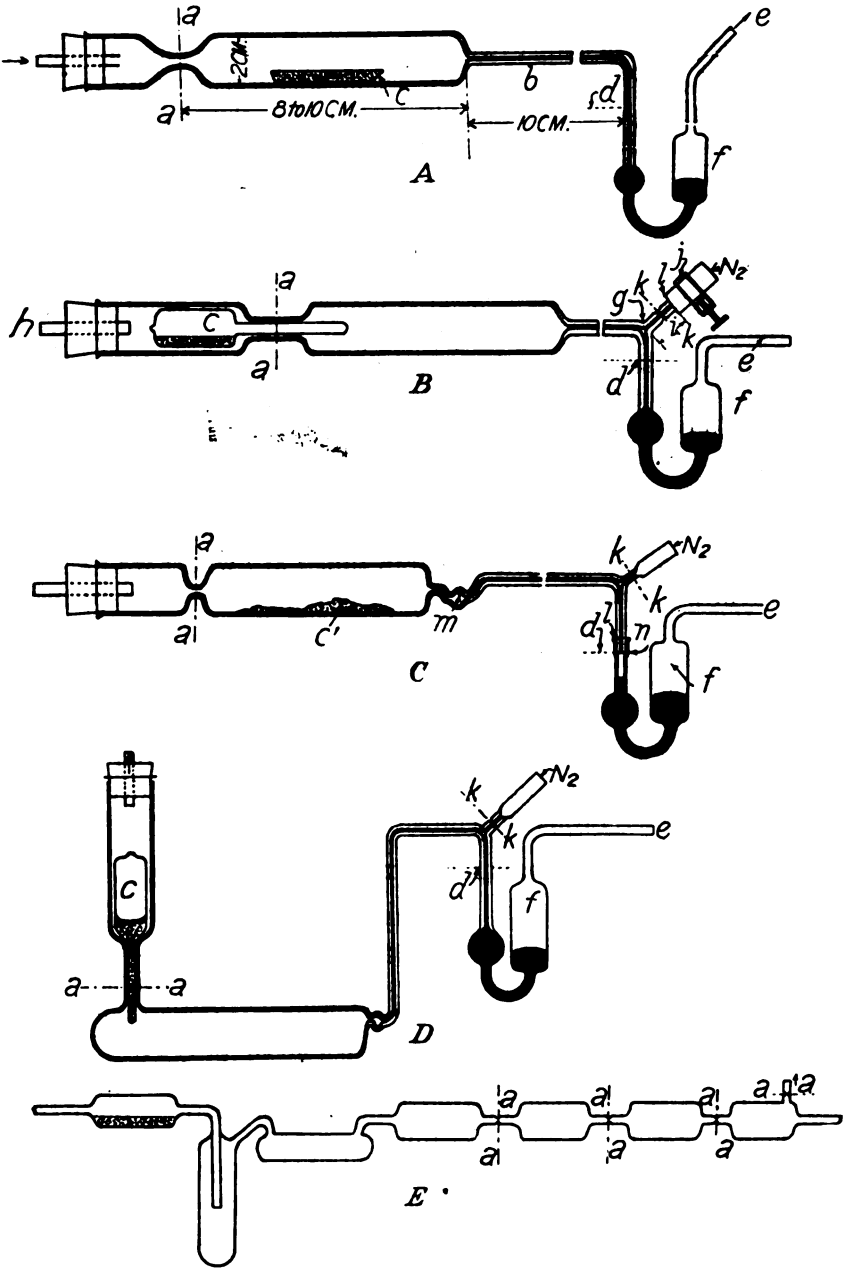

FIGURE 1.—Forms of containers, traps, and capsules: *A*, Pyrex container for nonhygroscopic chlorides; *B*, pyrex or silica container for hygroscopic chlorides; *C*, silica container for chlorides showing creeping tendency when fused; *D*, pyrex container for low-boiling chlorides used in oil bath; *E*, preparation capsules for formation, dehydration, and redistillation; *a–a*, points of sealing; *b*, capillary tube, 1 mm. diameter; *c*, boat or capsule containing chloride; *c'*, chloride in container; *d*, reading level; *e*, to manometer system; *f*, trap; *g*, point of sealing capillary tube to capillary outlet; *h*, exit of nitrogen; *i*, capillary outlet; *j*, pinchcock; *k–k*, constriction in capillary outlet; *l*, seal with de Khotinsky cement; *m*, bulb in capillary; *n*, end of silica capillary; N_2, entering gas

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tilting the trap end downward, and heating to fusion if necessary. The capsule *c*, when empty, was permitted to slip back in the enlarged rear end of the container, and the whole was sealed off by fusion at *a*–*a* and by the pinchcock at *j*. The capillary outlet at *i* was provided with a constriction at *k*–*k*, for sealing, but this closure was not made until after the evacuation of the tube. (See procedure below.)

The clear silica container used for the high temperature range, *c* (Fig. 1, *C*), differed in two ways from the container just described. A small bulb, *m*, was blown into the capillary near the container end. The bulb at this position prevented plugging of the capillary during the runs with very mobile chlorides by providing a reservoir for condensed vapors. Certain of the chlorides tended strongly to creep along the inner surface when fused; calcium chloride especially gave much trouble. The bulb retarded the flow into the capillary from this cause. The trap of the silica apparatus was usually made of pyrex glass and was not an integral part of the container. The silica capillary ending at *n* was ground off square and true on a lap and sealed into the snugly fitting trap tube *f* at *l* with hard de Khotinsky cement. Manipulation was the same as for the apparatus shown at *B*.

For certain of the low-boiling chlorides, such as arsenic and antimony, the container was heated in an electrically heated oil bath rather than in the tube furnace. For this work a pyrex container and trap, as in Figure 1, *D*, was used, which differed from previous types only in that both filling tube and capillary extended upward from the container, rather than directly outward.

MANOMETER AND ADJUNCTS

The manometer, shown diagrammatically in Figure 3, was of two arms of ordinary barometer tubing (4 mm. bore), the shorter arm (80 cm.) being directly sealed to various accessory tubes leading to the trap, and the longer arm (350 cm.) being open to the atmosphere. The manometer scales *v* were of cold-rolled steel, graduated directly in millimeters by comparison with a standard silver scale, and were provided with verniers reading to the tenth millimeter. Both scale and manometer tubes were carefully adjusted to the vertical, and the zeros of the scale brought to within 0.1 mm. of the same level. A leveling bulb, *w*, connected with the manometer system through a 3-way stopcock at *x* adjusted the mercury levels previous to or during a determination.

PRESSURE REGULATION

Pressure and vacuum between the trap and manometer were regulated from tanks connected to the system at *u* (short arm of the manometer) and by the accessory Sprengel pump j_1. For pressures

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down to about 6 cm., the tank p evacuated through valve o_4 by an ordinary water-suction pump q was satisfactory. For lower pressures the pump j_1 was used. For pressures above atmospheric, the small tank r was filled to 50 or 60 pounds pressure with gaseous carbon dioxide from the large tank s containing liquid carbon dioxide, through the 3-way cock t. Then s was closed off from the system at t, and v was connected through to the manometer. The valves o_2 and o_1 only were used to regulate, and had carefully ground needles and low-pitch feed screws. The pressure in the system could, with a little care, be controlled to within 0.2 mm. of a desired value.

FURNACE AND TEMPERATURE REGULATION

For the temperature range 300° to 1,300° C. an electric tube-furnace, such as is used for combustion work, was provided with a snugly fitted vitreosil protection tube, h. (Fig. 2, A.) The container cylinder was only large enough to permit three thermocouples (18-gauge chromel-alumel) to be inserted between the protection tube h and the container. The latter was placed as nearly as possible in the center of the furnace, the container being enough shorter than the furnace to insure a low-temperature gradient between the middle and ends. The actual gradient was closely determinable by keeping the thermocouples e at the middle and ends of the container f. Heat loss from the ends was minimized by plugging the ends of the protection tube with loose-fiber asbestos.

The thermocouples were passed through a cold-junction flask (Fig. 3); those leading to the ends of the container were connected with a S. & H. high-resistance deflection millivoltmeter, d, and the middle couple to a Leeds and Northrup portable potentiometer, c. The cold-junction flask e was provided with a calibrated thermometer, and the millivoltmeter and potentiometer had been previously calibrated. A correction curve for the thermocouple wire, as compared to standard chromel-alumel temperature-difference millivolts curves, was obtained by determination of the melting points of gold and silver; calibration of a five-multiple couple at the boiling point of water; and comparison with a standardized platinum and platinum-rhodium couple.

Temperature regulation was obtained by a variable voltage transformer with taps at 5-volt intervals from 100 to 150 volts, and with high and low resistance rheostats in the furnace circuit. Voltmeters a and ammeters b in this circuit facilitated regulation of a uniform energy input to the furnace.

For temperature ranges up to 300° C. the oil bath shown in Figure 2, B, was substituted for the tube furnace. The bath (Nujol oil) was provided with an electric heating coil, p, and a mechanical stirrer, n. Temperatures above 100° C. were obtained with a five-multiple couple,

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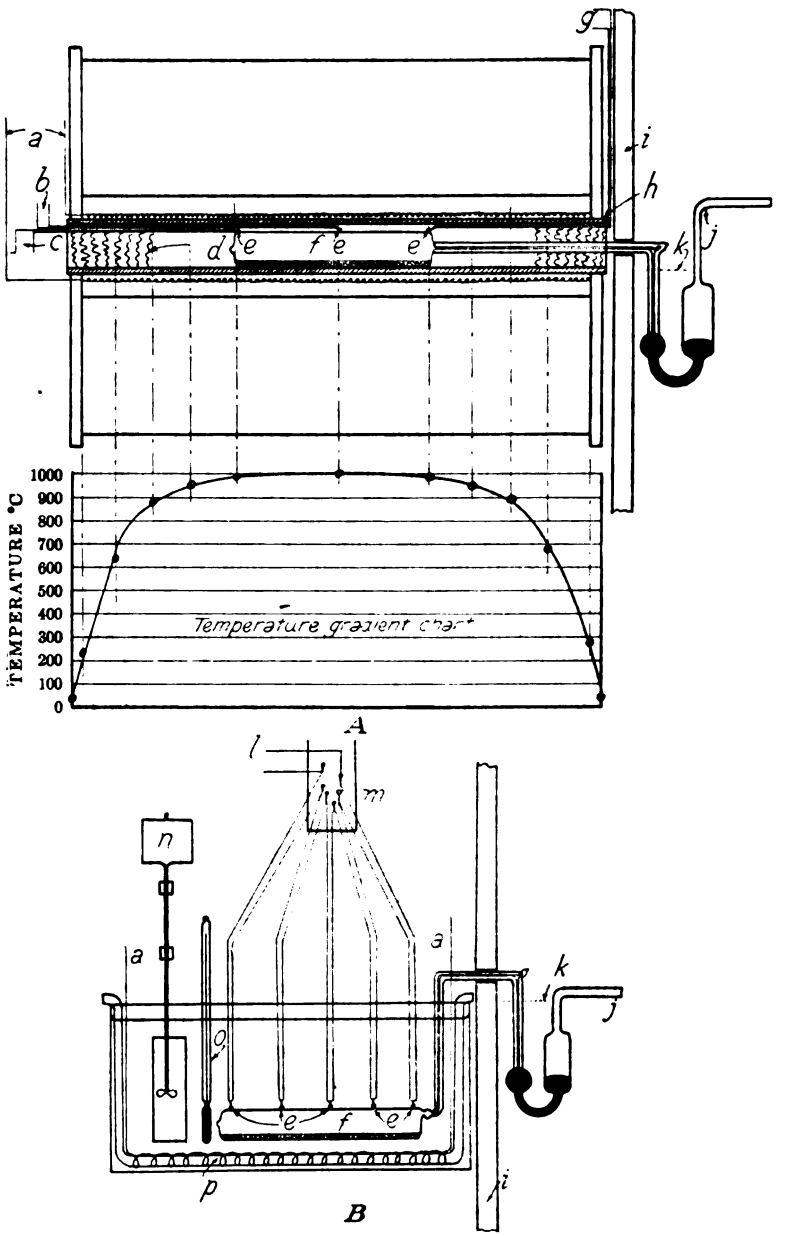

FIGURE 2.—Containers in position previous to experiment: *A*, In tube furnace with thermocouples (typical temperature gradient at 1,000° C.); *B*, in oil bath showing position of thermocouples; *a*, to power circuit; *b*, to cold junction and potentiometer; *c*, to cold junction and millivoltmeter; *d*, loose-fiber asbestos; *e*, thermocouples; *f*, container; *g*, to cold junction and millivoltmeter; *h*, silica protection; *i*, asbestos shield; *j*, to manometer system; *k*, reading level; *l*, to millivoltmeter and potentiometer; *m*, cold junction flask; *n*, motor stirrer; *o*, thermometer; *p*, heating coil

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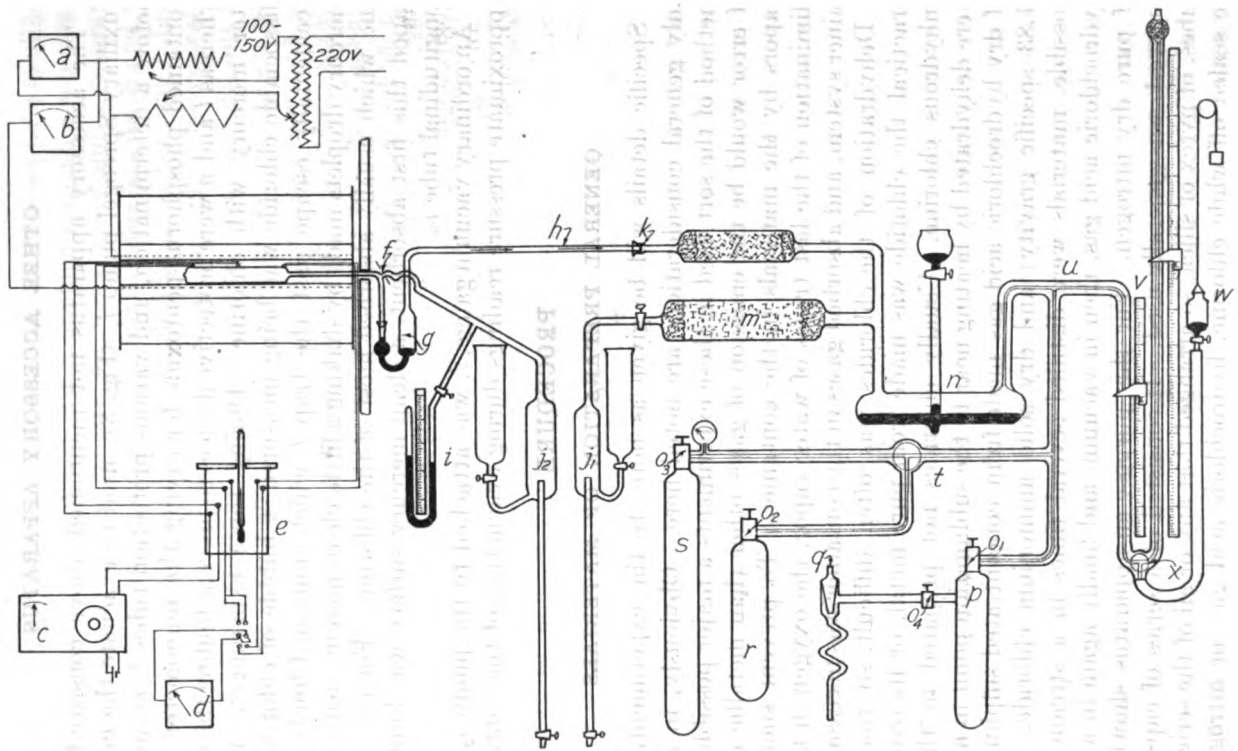

FIGURE 3.—Diagrammatic set-up of apparatus: *a*, Voltmeter; *b*, ammeter; *c*, potentiometer; *d*, high-resistance deflector millivoltmeter; *e*, cold junction box; *f*, constriction of capillary outlet; *g*, trap; *h*, to manometer system; *i*, vacuum gauge; j_1, Sprengel pump; j_2, pump; *k*, de Khotinsky seal; *l*, *m*, and *n*, protection tubes; *m*, PO_5;o_1 to o_4, valves; *p*, tank for pressures above 6 cm.; *q*, water-suction pump; *r*, small tank for pressures above atmospheric; *s*, liquid carbondioxide tank; *t*, 3-way cock; *u*, connection of tank to manometer system *v*. manometer scales; *w*, leveling bulb; *x*, 3-way stopcock

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with the hot junctions distributed uniformly along the container *f*, as shown; and up to 100° C. with a thermometer, *o* (Bureau of Standards calibration), reading to 0.1°.

OTHER ACCESSORY APPARATUS

The accessory apparatus not mentioned above consisted of the auxiliary Sprengel pump j_1 (Fig. 3), used to evacuate the container before a determination, and various protection tubes *l*, *m*, and *n*; *m* contained phosphorus pentoxide for drying the manometer system, whereas *l* and *n* were protective devices to prevent fouling the manometer mercury with chlorine. During those experiments where a dissociable chloride was being measured, a bubble of chlorine might accidentally escape past the trap *l*, which contained finely divided mercury droplets made by shaking a little clean mercury with calomel and which usually absorbed most of the chlorine. For any that escaped this first absorbent, a clean mercury surface was kept in the longitudinal tube *n*.

An ordinary vacuum gauge, *i*, was attached to the pump j_2 to give approximate pressure readings during evacuation of the container.

PROCEDURE

GENERAL PREPARATION OF MATERIALS

Specific details will be given as notes to the experimental data; only general considerations are noted here. Obviously, in a static method of the sort used in these experiments a major possible source of error would be the emission of gases other than metallic chloride vapors by the materials in the container. To prevent such error, elimination of the last traces of water vapor, the oxygen in the container system, and absorbed gases in the container was necessary.

Dehydration of the chlorides was often difficult, so that when practical the chloride was made from pure metal, or its oxide, and anhydrous chlorine. Usually chlorides not prepared in this way were dehydrated by heating near to the sublimation point in a stream of dry hydrochloric acid gas made from concentrated sulphuric acid (1.83 specific gravity) and dry solid ammonium chloride. Where possible, materials were distilled several times in a stream of dry hydrochloric acid gas, then in vacuum, and finally again in a stream of pure dry nitrogen. For this purpose an apparatus shown in *E*, Figure 1, was generally used. It consisted of a series of capsules or tubes, of pyrex or silica, so arranged that any or all of the series could be sealed off while chlorine, hydrochloric acid gas, or nitrogen was being passed through them. Each chamber, taken in order, served as a distillation bulb and the final sample was usually collected and sealed off in the next to last compartment.

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After the container from the capsule was filled, the container and contents were finally dried by heating to such a temperature that part of the material in the cylinder was distilled back into the enlarged rear end just before the final sealing of this end.

The nitrogen used in these experiments was obtained by a modification of the method of Lupton.[3] Air is bubbled through a solution of equal parts of 0.90 specific gravity ammonia water and a saturated solution of ammonium chloride. The mixed gases are dried and the carbon dioxide is removed by passage through a rather long column of soda lime. The gases are then passed through a heavy-walled pyrex tube (500° to 600° C.) packed with copper gauze. All but the first part of the copper should remain fairly clean. The gas is next passed through concentrated sulphuric acid to remove excess ammonia and through two bubblers in series containing alkaline pyrogallol, and is collected in large gas bottles with dilute alkaline pyrogallol as retaining liquid. In the outer bottle a layer of oil over the pyrogallol solution protects it from contact with the air. When the gas was to be used it was further purified by passage through fresh pyrogallol solution, then through concentrated sulphuric acid for drying. Last traces of hydrogen or oxygen were removed by passage through a heavy-wall pyrex tube (600°) containing copper oxide and clean bright copper gauze. Final drying was obtained by another passage through sulphuric acid and phosphorus pentoxide before the gas was used.

These rather elaborate precautions for the purification of nitrogen are necessary largely because nearly all of the metallic chlorides, especially in the presence of silica or glass, will react at high temperatures with even small amounts of oxygen, setting free a certain amount of chlorine. This liberation not only introduces error in pressure readings, but also fouls the mercury surface of the trap.

HANDLING CONTAINER BEFORE A DETERMINATION

The container was filled with nitrogen at slightly over atmospheric pressure, was sealed at the end opposite the trap, and was placed as shown in Figure 2 (p. 8) It was connected into the manometer system as in Figure 3 (p. 9), joining at k with hard de Khotinsky cement. The pinchcock on j in B, Figure 1, was opened, and evacuation of the container started immediately, using pump j_2. At the same time the vacuum valve o_1 was opened slightly, or else the pump j was started, in such a way as to balance the mercury levels of the trap. When the desired pressure (3 to 6 cm. Hg.) had been reached, the capillary outlet at f was sealed off, and the apparatus was ready for the run proper.

[3] Lupton, Sidney, Laboratory notes; preparation of nitrogen: Chem. News, vol. 33, 1876, p. 90.

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PROTECTION OF MERCURY IN THE TRAP

When chlorine was produced by thermal dissociation, apparatus without joints between the trap and container had to be used. The protection of the mercury surface in the trap under these conditions was a serious problem. The most satisfactory method was to cover the mercury surfaces with concentrated sulphuric acid of the strength having a minimum solubility for chlorine. The concentration most suitable was found to be 98.4 to 98.7 per cent H_2SO_4. A higher concentration has an appreciable SO_3 vapor pressure at ordinary temperatures, and attacks mercury rapidly, whereas a lower concentration has markedly higher solvent power for chlorine. A slight amount of chlorine is dissolved by this acid, but with a rather fine bore capillary for this part of the trap, and with a depth of 2 to 3 cm. of protective layer of acid, a blank determination on a tube containing chlorine at 1 atmosphere pressure to start and heated to 600° showed that the gas law was obeyed at constant volume to within about 0.5 per cent. This is within the experimental accuracy of the method.

The special sulphuric acid was made by redistilling fuming acid, condensing the sulphur trioxide evolved in the best obtainable concentrated acid, and after analysis of both the purified fuming acid and the concentrated acid, making up the desired concentration by mixture.

For details of procedure used in determining chlorine produced by thermal dissociation, see pages 52 to 54.

DETERMINATION

After the container had been evacuated and sealed as described, the pressure on the manometer side was slowly increased by opening valve o_2 until the mercury in the trap had risen in the capillary side to near the right-angle bend leading into the furnace. In those containers in which the trap was an integral part of the capillary, the position of the meniscus was adjusted to a fixed position by means of a reading telescope and cross hairs.

Ordinarily, however, the apparatus shown in *C*, Figure 1, was more satisfactory. The mercury column in the trap was not permitted to enter the capillary, but was adjusted until the meniscus was just in contact with the flat ground surface *n*, thus sealing the end of the capillary opening. This adjustment was so sensitive that no microscope was necessary. In this type of apparatus uncertain capillary depression corrections, discussed below, were reduced to a minimum, and the slight excess pressure required before the mercury would enter the capillary was a very welcome safeguard against shooting the mercury over into the container by incautious manipulation of the pressure valve.

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The manometer reading for this initial setting constituted the first recorded reading.

Current was now admitted to the heating elements of the furnace, or oil bath, so as to insure a slow steady temperature rise of approximately 200° per hour for the high-range experiments, and 50° per hour for the low. Continuous adjustment of the meniscus on the capillary side of the trap to its original fixed position was maintained by valve o_2, (Fig. 3). The increase in pressure due to the expansion of the nitrogen present, or to the formation of chloride vapor, was exactly balanced by adjustment of pressure on the manometer side of the trap. Readings of temperature and manometer were taken at appropriate intervals until the pressure had risen to a point indicating that the material was above its boiling point, or until the maximum temperature attainable by the furnace had been reached.

At the end of each determination, the temperature was permitted to drop slowly until the pressure in the container was near atmospheric, at which point the sealed-off capillary tip *f* was broken, admitting atmospheric pressure to the container. Readjustment of the pressure to bring the trap to its standard position during the run was now made, and the "blank" manometer reading taken. This pressure represents the sum of any capillary depression and correction due to different mercury levels in the trap. A barometer reading was made from an instrument with the same size tubing as the manometer and with similar scales.

METHOD OF CALCULATION

TEMPERATURE CORRECTIONS

The temperatures observed were taken from the ends and middle of the container tube. After suitable cold junction and calibration corrections were made as noted above, the temperatures for calculations, whether the middle, end, or some average should be chosen. In general, the middle temperature might range some 10° or 15° higher than the end when near 1,000°, with correspondingly less difference at lower temperatures.

Theoretically, it might be concluded that if, during vaporization of material in the container, there was a temperature difference between various parts of the container, the pressure reading could only be that corresponding to the lowest temperature. Vapor should be condensing at this point, and therefore be in equilibrium with the material in the container. This principle can not be accepted without question, however. Obviously, since a part of the container, namely the capillary, goes through all temperature ranges from the hottest part of the furnace to the outside room temperature, if equilibrium were actually obtained as supposed, the final result would be the immediate plugging of the capillary. Inasmuch as

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a determination requiring several hours heating could usually be completed without serious plugging, the condition mentioned evidently can not hold.

NOTE

Plugging of the capillary seldom took place with a capillary of about 1 mm. bore when the initial pressure was greater than 5 cm., due probably to the slowness of diffusion in the capillary. When, however, lower pressures were used at the start, the rate of diffusion became so rapid that an experiment could not be completed because of plugging.

A blank run on a tube containing only nitrogen gas showed that if the temperature chosen was taken as the average of the middle and mean end temperature, the closest approximation to the gas law was obtained. Consequently, this figure is recorded in the tables. The ratio of pressure to absolute temperature calculated on this basis for pure nitrogen was constant to within 0.36 per cent.

PRESSURE CALCULATION

If B is the barometer height, and H_2 and H_1 the heights of the mercury columns in the open and trap sides of the manometer respectively, the pressure between manometer and trap is obviously $B+(H_2-H_1)$. This pressure differs from that in the container, due to any difference in levels in the trap and capillary depressions due to difference in diameter between the sides of the trap. The two corrections are lumped together (H_t) by determining the manometer heights H'_2 and H'_1 when the pressure on the container side of the trap is a known value, usually atmospheric. In the latter case the total magnitude H_t is equal to $H'_2-H'_1$, and the gas pressure in the container is

$$\text{Observed pressure}=B+(H_2-H_1)-(H'_2-H'_1)$$

Since B, H'_2, and H'_1 are substantially constant during a determination, for purposes of calculation they are conveniently grouped together:

$$\text{Observed pressure}=[B-(H'_2-H'_1)]+(H_2-H_1).$$

No correction of pressure to a mercury column at 0° was made, inasmuch as any error introduced in this way, becoming zero for low pressures, would on the high range be less than pressure differences due to uncertainty of temperature readings. The temperature corresponding to the manometer scale is given for nearly all tests as the first recorded temperature in the tabulated data.

CALCULATIONS FROM PRESSURE AND TEMPERATURE READINGS

The experimental data are divisible into two major parts: A, Pressure and temperature readings below the point of detectable vapor

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pressure; and B, pressure and temperature readings above the point at which the pressure rises sharply.

If the gas law is written for condition A, $pv = nRT$ may be rearranged

$$p/T = nR/v = K,$$

where K is a constant in a given determination dependent on the original pressure of nitrogen at the start of the run, and on the volume of the container. R is the gas constant, v is maintained constant by the manipulation of the experiment, and n is constant as long as the materials of the container or those in it are not producing vapor. In general, from four to eight readings of the pressure and temperature were taken in an experiment before the point of vaporization had been reached. The constancy of calculated values of K during this temperature range constituted a valuable check on the purity of materials in the container. If K showed a marked rise at temperatures at which it was known from observation during the preparation of the sample that no appreciable vapor pressure existed, insufficient dehydration or the presence of some impurity or leak was denoted and the determination rejected. In satisfactory determinations the value of K was usually constant to better than 0.5 per cent.

As soon as K began to rise rapidly due to vaporization, after previous constancy as under condition A, the calculation of K was discontinued. Because of the logarithmic form of the vapor-pressure temperature curve, the point at which vaporization begins is quite sharply demarked. Obviously, from this point of departure, n in the gas law is no longer constant for these conditions, so that an average value of K from previous determinations was used to calculate the pressure in the container due to inert gas only, taking the temperature corresponding to each pressure observation separately as

$$\text{Pressure calculated} = K_{\text{average}} \times T.$$

To save space not all the data for the determination of K are given in the tables. The first recorded data, however, show the number of determinations of K, the average value and its average deviation from the value given, and the temperature range over which the value was determined.

The vapor pressure of the material in the container is easily calculated as

$$\text{Vapor pressure} = \text{pressure observed} - \text{pressure calculated}.$$

The tables of data contain, besides the above, columns showing the common logarithm of the pressure of vapor expressed in centimeters of mercury, and reciprocal values of absolute temperature multiplied by 10^3, for convenience in plotting in the usual way.

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EXPERIMENTAL RESULTS

Determinations made on the vapor pressure of the metallic chlorides included here have been more or less arbitrarily grouped into three classes: Group I covered monovalent metal chlorides. Determinations were made on LiCl, NaCl, Cu_2Cl_2 (CuCl), AgCl, and $NaAgCl_2$.

Group II covered divalent metal chlorides. Determinations were made on $ZnCl_2$, $CdCl_2$, $BaCl_2$, $CaCl_2$, $MgCl_2$, $PbCl_2$, $MnCl_2$, $FeCl_2$, $NiCl_2$, $CoCl_2$, $CuCl_2$, and $SnCl_2$.

Group III: Covered trivalent metal chlorides. Determinations were made on $AlCl_3$, $FeCl_3$, $AsCl_3$, $SbCl_3$, $BiCl_3$.

GROUP I. MONOVALENT METAL CHLORIDES

The chlorides of the alkali metals and of silver and cuprous copper seem to have appreciable vapor pressures through about the same temperature limits, and the results are therefore plotted together. The plots also include the available determinations of other investigators as noted. Limitations of the maximum attainable temperatures in these experiments prevent them from covering as wide a range of measurable pressures as would be desirable, consequently the results are somewhat less satisfactory than the determinations on the divalent metal chlorides.

LITHIUM CHLORIDE

Experimental data ..... Table 1.
Logarithmic plot ..... Figure 4.

TABLE 1.—*Data on vapor pressures of lithium chloride (LiCl) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs.
1 to 13	23.8 to 821.0		(K. $10^{\frac{1}{2}}$=4.71±0.01)				
14	881.1	1,154.2	5.84	5.44	0.40	−0.398	866.5
15	930.0	1,203.1	6.80	5.67	1.13	+.353	831.2
16	989.6	1,262.7	8.29	5.95	2.34	.3692	792.0
17	1,023.4	1,296.5	9.78	6.11	3.67	.5646	771.2
18	1,080.5	1,353.6	12.92	6.37	6.55	.8161	739.0
19	1,130.4	1,403.5	16.56	6.61	9.95	.9978	712.8
20	1,143.7	1,416.8	18.05	6.67	11.38	1.0561	705.8
21	1,160.9	1,434.0	19.61	6.80	12.81	1.1077	697.7
22	1,218.0	1,491.1	20.31	7.02	13.29	1.1233	671.0
23	1,252.0	1,525.4	20.49	7.18	13.31	1.1243	655.5

PREPARATION

Lithium carbonate (c. p.) was ignited in a platinum dish to destroy traces of organic matter and to drive off volatile material. The residue was dissolved in c. p. hydrochloric acid, and the solution decanted from traces of insoluble material and evaporated to dryness with excess hydrochloric acid in a platinum dish. The solid material was placed in a silica container (Fig. 3, p. 5), dehydrated, and partly distilled first in anhydrous hydrochloric acid gas, then in dry nitrogen.

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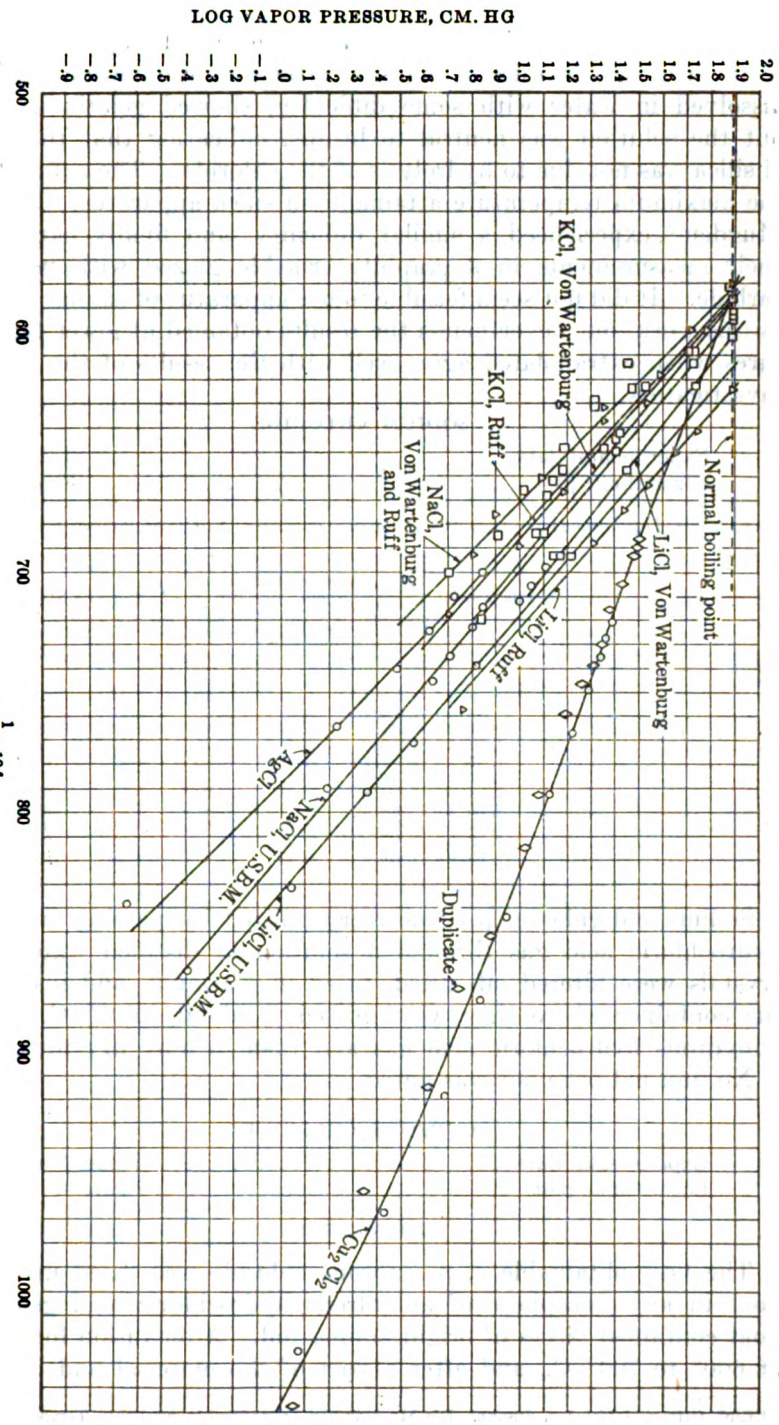

FIGURE 4.—Logarithmic plot of vapor pressures of chlorides of the alkali metals (lithium, sodium, and potassium), silver, and cuprous copper: □, Von Wartenburg; △, Ruff and Mugdan; O, author's values; ◇, author's duplicate

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NOTES ON DETERMINATION

Fused lithium chloride is rather active in dissolving silica at high temperatures. Samples of material after a determination, on being dissolved in water with some difficulty, showed gelatinous silica, but the solution was neutral to litmus, indicating that the attack of silica was not due to hydrolysis of the chloride. The action limits the maximum temperature attainable in silica apparatus. Ruff and Mugden [3] experienced a similar difficulty, and finally carried out their measurements in a graphite crucible glazed with vanadium carbide. It did not seem feasible to use apparatus of similar material in this work, but nevertheless the results obtained at lower temperatures when extrapolated agree well with the results of the previous investigators.

SODIUM CHLORIDE

Experimental data ..... Table 2.
Logarithmic plot ..... Figure 4.

TABLE 2.—*Data on vapor pressures of sodium chloride (NaCl) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T_{abs}}10^3$
1 to 9	22.4 to 672.6			(K. 10^3=2.242±0.011)			
10	746.9	1,020.0	23.13	22.89	0.24	−0.620	980.5
11	807.3	1,080.4	24.63	24.26	.37	−.432	925.5
13	992.3	1,265.4	29.92	28.40	1.52	+.182	790.0
15	1,050.5	1,323.6	32.95	29.70	3.25	.512	755.8
16	1,069.1	1,342.2	34.41	30.10	4.31	.635	745.0
17	1,087.4	1,360.5	35.54	30.51	5.03	.702	735.2
18	1,110.8	1,383.9	37.38	31.02	6.36	.804	722.8
19	1,127.1	1,400.2	38.59	31.41	7.18	.856	714.0
20	1,135.2	1,408.3	39.71	31.60	8.11	.909	710.2
21	1,144.0	1,417.1	40.31	31.78	8.53	.931	705.8
22	1,146.9	1,420.0	41.12	31.86	9.26	.966	704.1

Sodium chloride (c. p.) was recrystallized by passing anhydrous hydrochloric acid gas through a solution in distilled water. The crystals were filtered off, dried, fused in platinum, and inserted in the container where they were heated to about 1,000° C., first in anhydrous hydrochloric acid gas and then in pure dry nitrogen.

No unusual behavior was noted.

CUPROUS CHLORIDE

Experimental data ..... Tables 3 and 4.
Logarithmic plot ..... Figure 4.

PREPARATION

The best obtainable c. p. cuprous chloride was fused in a silica boat in an atmosphere of anhydrous hydrochloric acid gas. The boat contained pieces of bright copper foil. After fusion for 2 hours at 600° to 700° C., and after a part of the material had been dis-

[3] Ruff, Otto, and Mugden, Susanne, Die Messung von Dampfdruken bei hohen Temperaturen und die Dampfdruke der Alkalihalogenide: Ztschr. anorg. Chem., Bd. 117, 1921, pp. 147–171.

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tilled from the boat, the material was put into the container shown in Figure 1, *B*, and reheated to 600° C. in hydrochloric acid gas and in nitrogen. The copper remained with the chloride during the determination. The material was nearly pure white when cool.

NOTES ON DETERMINATION

The presence of metallic copper during preparation and determination was essential. The first determination was made without copper and was unsatisfactory due to the evolution of chlorine, as indicated by the tarnishing of the mercury meniscus of the trap. The action was probably due to traces of cupric salts. For further comment concerning cuprous and cupric copper as chlorides, see the determination of the latter and especially the notes on pages 52 to 54.

The determination on cuprous copper gave results rather widely at variance with boiling-point determinations found in the handbooks, hence duplicate determinations seemed desirable. The logarithmic plot shows that although the results at low temperatures show a slight difference, the agreement becomes almost perfect at higher temperatures, so that the boiling point of the material can not be far from the value found. It should be noted, however, that the cuprous chloride was in contact with metallic copper. No definite data were found in the literature relative to this solubility, nor could such data be obtained experimentally during the present work. The matter should be investigated before the values given are accepted without reservation.

TABLE 3.—*Data on vapor pressures of cuprous chloride (Cu_2Cl_2) at various temperatures*

Test No.	Temperature, ° C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$
1 to 6	24.2 to 631.5		(K. 10^3=2.330±0.008)				
7	703.2	976.3	23.95	22.75	1.20	0.0791	1,024.5
8	761.6	1,034.7	26.75	24.10	2.65	.4231	967.2
9	815.6	1,088.7	30.14	25.35	4.79	.6802	919.0
10	864.5	1,137.6	33.29	26.50	6.79	.8319	879.2
11	912.4	1,185.5	36.47	27.62	8.85	.9470	843.3
12	952.1	1,225.2	39.49	28.53	10.96	1.0398	816.0
13	988.4	1,261.5	42.64	29.39	13.25	1.1253	792.8
14	1,031.7	1,304.8	46.71	30.40	16.31	1.2143	767.0
15	1,061.8	1,334.9	50.56	31.08	19.48	1.2896	749.3
16	1,088.6	1,361.7	53.71	31.62	22.09	1.3440	734.3
17	1,103.1	1,376.2	55.34	32.09	23.25	1.3663	726.5
18	1,114.3	1,387.4	57.12	32.32	24.80	1.3942	720.7

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TABLE 4.—*Data on vapor pressures of cuprous chloride (Cu_2Cl_2; duplicate) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^6$
1 to 5	28.8 to 572.1		(K. 10^3=2.842±0.004)				
6	682.5	955.6	28.29	27.17	1.12	0.0481	1,046.5
7	771.4	1,044.5	31.91	29.68	2.23	.3483	958.0
8	819.3	1,092.4	34.83	30.74	4.09	.6119	915.3
9	871.9	1,145.0	38.28	32.53	5.75	.7596	873.3
10	900.7	1,173.8	41.06	33.33	7.63	.8827	852.2
11	954.0	1,227.1	45.41	34.90	10.51	1.0217	814.7
12	988.5	1,261.6	48.21	35.87	12.34	1.0911	792.5
14	1,043.5	1,316.6	53.27	37.43	15.84	1.1996	759.5
15	1,066.9	1,340.0	57.02	38.10	18.92	1.2769	746.2
16	1,084.7	1,357.8	59.43	38.60	20.83	1.3190	737.0
17	1,100.2	1,373.3	61.56	39.03	22.53	1.3530	728.5
18	1,123.2	1,396.3	64.20	39.70	24.50	1.3890	716.0
19	1,146.2	1,419.3	67.48	40.32	27.16	1.4338	704.8
20	1,169.1	1,442.2	71.03	41.00	30.03	1.4776	693.0
21	1,176.9	1,450.0	72.61	41.22	31.39	1.4966	689.8
22	1,184.8	1,457.9	73.63	41.41	32.22	1.5083	686.0

SILVER CHLORIDE

Experimental data ..... **Table 5.**
Logarithmic plot ..... **Figure 4.**

PREPARATION

Silver chloride was precipitated in the dark from boiling solutions of equivalent amounts of silver nitrate and sodium chloride, both c. p. reagents. The precipitate was washed 10 times by decantation with several liters of boiling distilled water, collected in a glass tube without filtration (by settling only), and compressed by a glass plunger into cylindrical pellets 1 cm. in diameter and about 2 cm. long. Filtration is to be avoided because traces of paper or organic matter make it impossible to prevent decomposition on dehydration. The pellets were dried in the dark in a desiccator, first over concentrated sulphuric acid, then over phosphorus pentoxide. Pellets dried in this way could be fused in a silica container in the light without forming metallic silver, or even incipient darkening. Obviously no dissociation or hydrolysis was taking place. The fused material was pearly white, and showed no nuclei of reduced material under high magnification.

NOTES ON DETERMINATION

Silver chloride gave no evidence of thermal dissociation during the run, for the mercury surface remained entirely brilliant and the material after cooling had not visibly changed when examined under high magnification. Unfortunately, the vapor pressure of silver chloride is so low at the maximum attainable temperature of these experiments that only a few points of the curve were obtainable. The curvature at the lower end of the logarithmic plot, influenced by one point only, is quite uncertain because of the inaccuracy of the method at low pressures.

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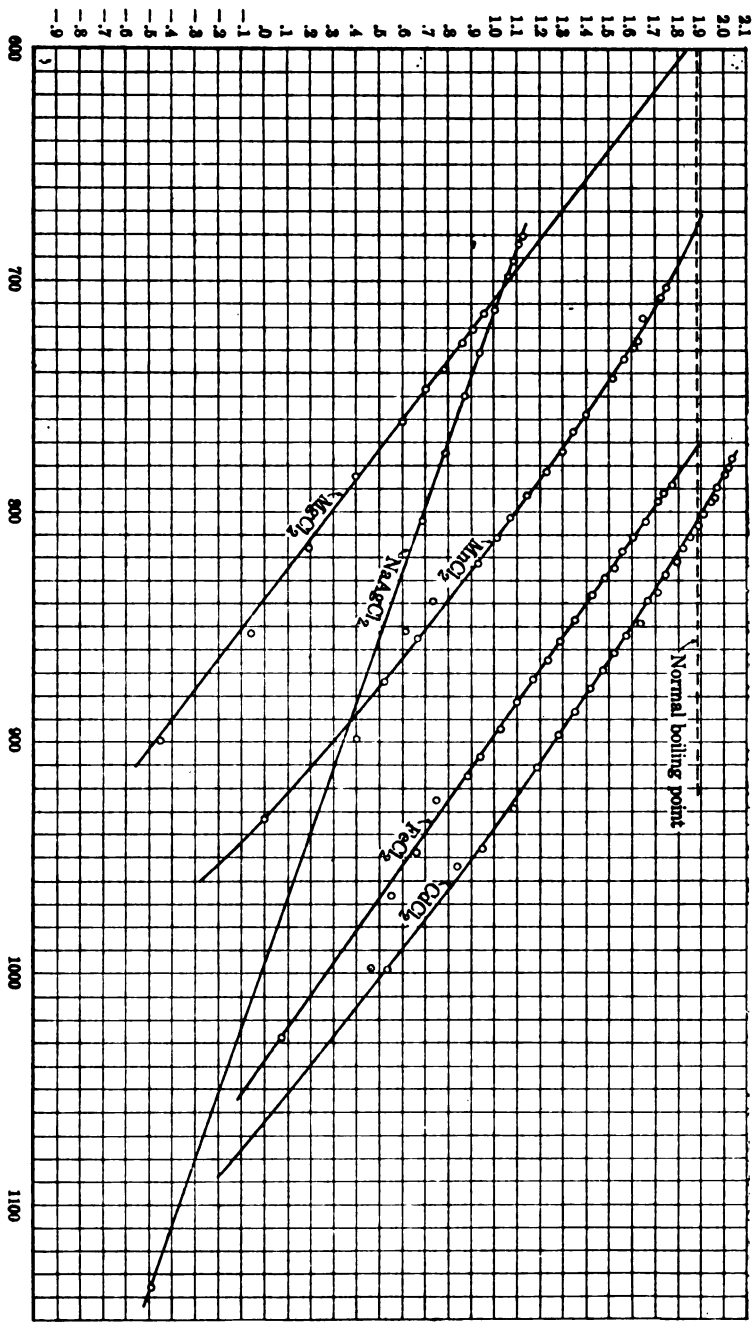

FIGURE 5.—Logarithmic plot of vapor pressures of chlorides of magnesium, sodium silver, manganese, cadmium, and ferrous iron

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TABLE 5.—*Data on vapor pressures of silver chloride (AgCl) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, c. m Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$
1 to 10	20.2 to 772.7		(K. 10^3=2.257±0.006)				
11	854.3	1,127.4	25.72	25.42	0.30	−0.523	887.0
12	933.9	1,207.0	27.46	27.22	.24	−.630	828.5
13	1,035.6	1,308.7	31.17	29.50	1.67	.223	764.5
14	1,077.2	1,350.3	33.49	30.46	3.03	.481	740.3
15	1,108.3	1,381.4	35.25	31.18	4.07	.610	723.8
16	1,136.0	1,409.1	37.08	31.78	5.25	.720	710.0
17	1,155.9	1,429.0	39.37	32.30	7.07	.849	699.8

SODIUM-SILVER CHLORIDE

Experimental data ..... Table 6.
Logarithmic plot ..... Figure 5.

PREPARATION

Equimolal parts of silver and sodium chloride prepared as for silver chloride were fused together in silica in an atmosphere of dry nitrogen.

NOTES ON DETERMINATION

Although the freezing-point determinations of Sandonini [4] and Botta [5] do not show definite data proving the existence of the double salt $NaAgCl_2$ in fused mixtures, certain peculiarities in the vaporization of silver and sodium chlorides in the chloridizing roast of silver ores, as well as definite knowledge that the double salt exists in solution (solubility of silver chloride in brine) made this determination of considerable interest.

The data obtained seem to show that the double salt does exist at fairly high temperatures, and has a definite vapor pressure at temperatures somewhat lower than either for sodium or silver chlorides that is greater than the sum of the vapor pressures of the pure materials at a definite temperature. The apparent heat of vaporization also differs markedly from that of other monovalent metal chlorides.

TABLE 6.—*Data on vapor pressures of sodium-silver chloride ($NaAgCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^4$ abs
1 to 10	24.0 to 873.1		(K. 10^3=3.316±0.006)				
11	971.9	1,245.0	46.15	41.28	4.87	0.687	803.2
12	1,019.6	1,292.7	49.01	42.83	6.18	.791	773.7
13	1,061.5	1,334.6	51.65	44.21	7.44	.871	749.7
14	1,094.7	1,367.8	53.92	45.35	8.57	.933	731.2
15	1,130.9	1,403.0	56.52	46.50	10.02	1.001	712.7
16	1,156.9	1,430.0	58.91	47.41	11.50	1.061	699.2
17	1,172.8	1,445.9	60.21	47.90	12.31	1.091	691.8
18	1,188.7	1,461.8	61.61	48.47	13.14	1.119	684.0
19	1,195.3	1,468.4	62.43	49.00	13.43	1.129	681.3

[4] Sandonini, Carlo, Analisi termica di miscele binarie dei clorure di metalli monovalenti: Rend. Reale accad. Lincei, ser. 5, vol. 23, pt. I, May 21, 1911, pp. 758–764.

[5] Botta, W., Ueber Mischkristalle aus Chlornaturium und Chlorsilber (Huantajayit): Centralb. für Mineral., Geol., u. Paläontol., Mar. 1, 1911, pp. 128–139.

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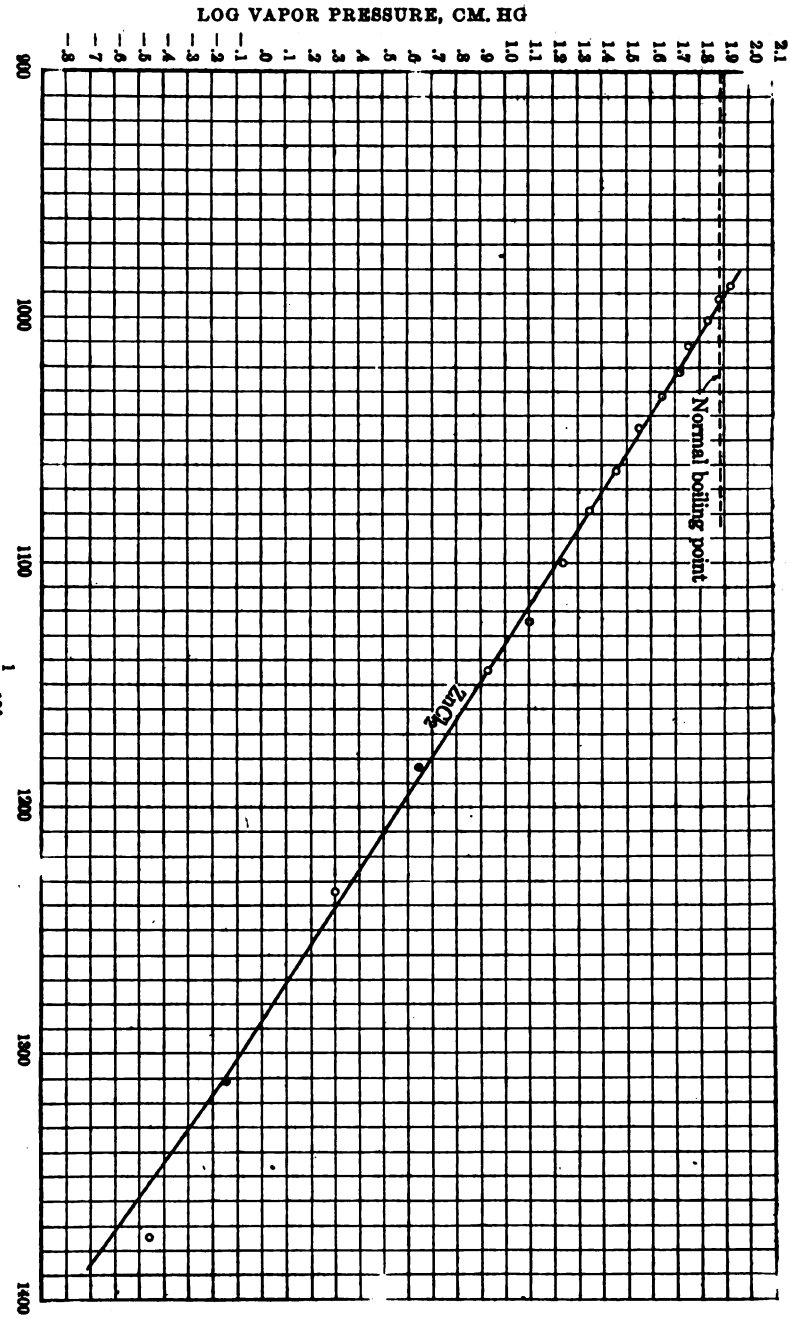

FIGURE 6.—Logarithmic plot of vapor pressures of zinc chloride

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GROUP II. DIVALENT METAL CHLORIDES

With the exception of the alkaline earth metals, it was possible to approach near to, or even somewhat above, the normal boiling points of the divalent metal chlorides. The results are thought to be the most satisfactory determinations of the work.

ZINC CHLORIDE

Experimental data ..... Table 7.
Logarithmic plot ..... Figure 6.

PREPARATION

The method used for the preparation of zinc chloride, so far as is known, has not previously been described. The action of chlorine on metallic zinc was found difficult to carry out, as the chloride tended to dissolve the metal.

Dry chlorine gas was passed over c. p. anhydrous zinc oxide at 600° to 700° C. in a silica tube. The zinc chloride condensed from the gases produced in the reaction was redistilled, first in chlorine, then twice in vacuum (0.5 cm. Hg.), and finally in dry nitrogen. During the entire process the material never came in contact with air, as samples were preserved in sealed capsules. The product was very pure (free from oxide and hydrochloric acid) and showed no residue when completely distilled. When it cooled rapidly from the molten state, it easily solidified as a clear glasslike solid, which gradually became crystalline after standing some weeks or months.

NOTES ON DETERMINATION

There was no evidence of thermal dissociation. Zinc chloride has quite definite curvature of the logarithmic plot, which indicates a relatively high change of heat of vaporization with the temperature.

TABLE 7.—*Data on vapor pressures of zinc chloride ($ZnCl_2$) at various temperatures*

Test No.	Temperature, ° C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^4$ abs
1 to 6	28.7 to 412.7		(K. 10^3=2.609±0.010)				
7	454.2	727.3	19.23	18.96	0.27	−0.5686	1,375.5
8	489.9	763.0	20.47	19.89	.58	− .2366	1,311.0
9	537.8	810.9	23.10	21.13	1.97	+ .2943	1,234.0
10	572.4	845.5	26.48	22.03	4.45	.6483	1,183.0
11	601.7	874.8	31.25	22.81	8.44	.9262	1,144.0
12	616.5	889.6	35.69	23.20	12.49	1.0966	1,124.5
13	636.3	909.4	40.86	23.21	17.65	1.2470	1,100.0
14	654.2	927.3	47.11	24.19	22.92	1.3603	1,078.5
15	668.7	941.8	53.49	24.56	28.93	1.4614	1,062.0
16	684.1	957.2	61.30	24.97	36.33	1.5603	1,045.0
17	695.8	968.9	69.13	25.28	43.85	1.6420	1,032.5
18	706.0	979.1	78.16	25.53	52.63	1.7213	1,021.5
19	716.2	989.3	87.30	25.80	61.50	1.7690	1,011.0
20	724.9	998.0	94.62	26.03	68.59	1.8360	1,002.0
21	734.3	1,007.4	102.85	26.28	76.57	1.8840	992.8
22	739.5	1,012.6	110.86	26.41	84.45	1.9268	987.8

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CADMIUM CHLORIDE

Experimental data ..... Table 8.
Logarithmic plot ..... Figure 5.

TABLE 8.—*Data on vapor pressures of cadmium chloride ($CdCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^6$ abs
1 to 5	24.1 to 575.7			(K. 10^3=3.66±0.05)			
6	728.4	1,001.5	7.02	3.67	3.35	0.5250	998.7
7	765.3	1,038.4	10.52	3.80	6.72	.8274	953.7
8	784.0	1,057.1	12.85	3.86	8.99	.9538	946.0
9	802.8	1,075.9	16.15	3.93	12.22	1.0871	929.5
10	824.7	1,097.8	19.48	4.01	15.47	1.1894	911.2
11	841.9	1,115.0	23.51	4.09	19.42	1.2881	896.7
12	854.5	1,127.6	26.95	4.13	22.82	1.3584	886.8
13	867.6	1,140.7	30.50	4.18	26.32	1.4206	876.5
14	878.3	1,151.4	34.29	4.22	30.07	1.4780	868.5
15	888.0	1,161.1	37.46	4.26	33.20	1.5210	861.2
16	897.9	1,171.0	42.24	4.30	37.94	1.5790	853.8
17	905.4	1,178.5	47.70	4.31	43.39	1.6371	848.4
18	920.0	1,193.1	52.00	4.36	47.64	1.6780	838.3
19	922.7	1,195.8	56.25	4.38	51.87	1.7150	836.0
20	935.3	1,208.4	61.34	4.42	56.92	1.7550	827.8
21	942.8	1,215.9	66.68	4.45	62.23	1.7942	822.0
22	953.2	1,226.3	71.31	4.49	66.82	1.8252	815.3
23	959.7	1,232.8	75.92	4.52	71.40	1.8538	811.0
24	968.3	1,241.4	81.18	4.55	76.63	1.8846	805.3
25	976.1	1,249.2	86.98	4.57	82.41	1.9160	800.6
26	982.7	1,255.8	92.40	4.60	87.80	1.9435	796.0
27	986.7	1,259.8	95.99	4.61	91.38	1.9608	794.3
28	993.6	1,266.7	99.13	4.64	94.49	1.9753	789.3
29	1,002.8	1,275.9	105.90	4.67	101.23	2.0054	783.8
30	1,007.9	1,281.0	109.16	4.70	104.46	2.0188	780.3
31	1,012.8	1,285.9	112.21	4.71	107.50	2.0311	777.6

PREPARATION

Some very pure cadmium (99.96), that had been specially purified by repeated electrodeposition from a rather strong acid solution was obtained through the courtesy of Mr. J. F. Cullen, of the Midvale smelter of the United States Smelting & Refining Co. This material was treated with dry chlorine at 600° to 700° C. until all the metal was converted. There are three liquid phases produced between cadmium chloride and the metal during a part of the action, probably due to the solubility of the metal in chloride, consequently the action must be continued for a considerable period until only colorless chloride remains. The chloride was further heated in a vacuum (0.5 cm.) for 2 hours at 700° to remove possible dissolved chlorine, and finally heated to incipient distillation in a stream of dry nitrogen and preserved in a sealed capsule. It was never in contact with air, though it is less hygroscopic than the zinc chloride.

NOTES ON DETERMINATION

No thermal dissociation was noted. The heat of vaporization changes with temperature similarly as with the zinc salt.

BARIUM CHLORIDE

Experimental data ..... Table 9.
Logarithmic plot ..... Figure 7.

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PREPARATION

Barium chloride (c. p.) was fused in an atmosphere of anhydrous hydrochloric acid gas, and further heated at 1,100° C. in a stream of dry nitrogen.

TABLE 9.—*Data on vapor pressures of barium chloride ($BaCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$
1 to 10	21.0 to 987.5			$K.10^3=4.93\pm0.03$			
11	1,060.8	1,342.9	5.74	5.67	0.07	−1.155	745
12	1,162.1	1,435.2	6.51	6.07	.44	− .357	697
13	1,192.8	1,465.9	6.82	6.20	.62	− .208	683
14	1,213.6	1,486.7	7.13	6.28	.85	− .071	674

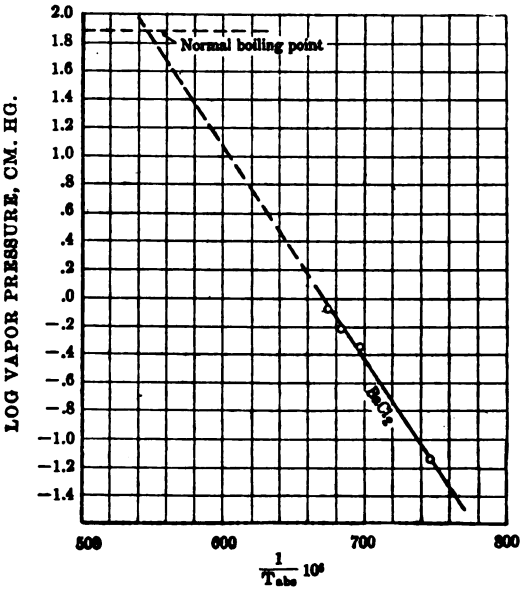

FIGURE 7.—Logarithmic plot of vapor pressures of barium chloride

NOTES ON DETERMINATION

Barium chloride has an extremely low vapor pressure at temperatures obtainable in the present work. The value of K in Table 9, remaining constant up to 987.5° C., shows no vapor formed up to this point. Four subsequent readings were taken, as shown in the table and plot, but the inaccuracy, with such small differences between observed and calculated values of pressure, must be great, and probably the readings of vapor pressure obtained are not dependable, although they do seem to lie on a straight line when plotted.

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CALCIUM CHLORIDE

Experimental data___ Table not given.
Logarithmic plot_____ No measurable vapor pressure at 1,200° C.

PREPARATION

Calcium chloride (c. p.) was dehydrated by fusion in silica in an atmosphere of anhydrous hydrochloric acid gas. The sample was subsequently heated to 1,100° C. in a stream of dry nitrogen.

NOTES ON DETERMINATION

No tabulated data are shown for calcium chloride, inasmuch as it was not possible to detect any measurable vapor pressure. Deviation in the pressure-temperature relations of the gas in the container from the normal gas law was not greater than the probable experimental error. When the container was heated from 24° to 1,137° C., nineteen pressure-temperature readings were taken, with the result:

$$\text{Average } K.10^2 = 4.49 \pm 0.05 \text{ (19 readings)}$$

Over the range 421° to 1,137° C., the variation was less:

$$\text{Average } K.10^2 = 4.52 \pm 0.03 \text{ (15 readings)}$$

The maximum possible deviation involved in the above values of K corresponds to about 0.4 cm., assuming absolute accuracy of temperature, therefore no vapor pressure greater than 0.4 cm. can exist for calcium chloride below 1,137° C. Any less vapor pressure could obviously not be detected with certainty in these experiments.

MAGNESIUM CHLORIDE

Experimental data ..... Table 10.
Logarithmic plot..... Figure 5.

TABLE 10.—*Data on vapor pressures of magnesium chloride ($MgCl_2$) at various temperatures*

Test No.	Temperature, ° C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs
1 to 9	28.8 to 704.7			$K.10^2 = 3.848 \pm .025$			
10	782.9	1,056.0	40.74	40.64	0.10	−1.000	946.3
11	838.7	1,111.8	43.10	42.75	.35	−.456	899.5
12	899.8	1,172.9	45.97	45.10	.87	−.061	852.7
13	952.3	1,225.4	48.70	47.13	1.57	.196	816.0
14	1,000.7	1,273.8	51.46	48.97	2.49	.396	785.2
15	1,040.7	1,313.8	54.50	50.52	3.98	.600	761.5
16	1,065.7	1,338.8	56.45	51.43	5.02	.701	747.0
17	1,084.8	1,357.9	58.39	52.22	6.17	.790	737.0
18	1,103.5	1,376.6	60.35	52.93	7.42	.870	726.3
19	1,115.5	1,388.6	61.54	53.40	8.14	.910	720.8
20	1,127.4	1,400.5	62.92	53.88	9.04	.956	714.0

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PREPARATION

Magnesium chloride (c. p.) was dried and fused in a stream of anhydrous hydrochloric acid gas, and subsequently heated to 1,000° in dry nitrogen.

NOTES ON DETERMINATION

No unusual behavior was noted, except that the value of K was slightly less constant than usual, which may render the vapor pressure values calculated somewhat less certain than in the more satisfactory determinations. There was no evidence of thermal dissociation.

LEAD CHLORIDE

Experimental data ..... Table 11.
Logarithmic plot ..... Figure 8.

PREPARATION

Lead chloride (c. p.) was recrystallized twice from 0.1 normal hydrochloric acid, dehydrated in a stream of anhydrous hydrochloric acid gas, and finally heated to the beginning of distillation in dry nitrogen.

NOTES ON DETERMINATION

The determination on lead chloride was undertaken largely as a check on the method by comparison with the results of Eastman and Duschak.[6] The comparison is seen to be excellent on the higher range. The difference in method probably accounts for the slight differences at lower temperatures, both in pressures and heats of vaporization. It seems probable that the present results, showing slightly higher values of vapor pressure at lower temperatures, were obtained with a more completely saturated vapor phase.

TABLE 11.—*Data on vapor pressures of lead chloride ($PbCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs
1 to 10	25.5 to 548.7			($K.10^3=8.75\pm0.04$)			
11	607.7	880.8	8.03	7.71	0.32	−0.4949	1,135.5
12	682.4	955.5	10.41	8.36	2.05	.3116	1,046.5
13	719.0	992.1	12.37	8.68	3.69	.4297	1,008.0
14	748.1	1,021.2	15.02	8.94	6.08	.7838	979.3
15	831.0	1,104.1	27.05	9.65	17.40	1.2906	906.2
16	871.4	1,144.5	39.18	10.00	29.18	1.4649	874.2
17	883.6	1,156.7	43.55	10.11	33.44	1.5242	864.3
18	926.4	1,199.5	66.22	10.49	55.73	1.7580	834.0
19	949.9	1,222.0	84.33	10.70	73.63	1.8670	818.0
20	971.0	1,244.1	97.97	10.89	87.08	1.9399	804.1
21	979.1	1,252.2	107.78	10.97	96.81	1.9860	798.5
22	990.0	1,263.1	119.27	11.06	108.21	2.0342	792.0
23	993.2	1,266.3	119.39	11.07	108.32	2.0346	790.0

[6] Eastman, E. D., and Duschak, L. H.; work cited.

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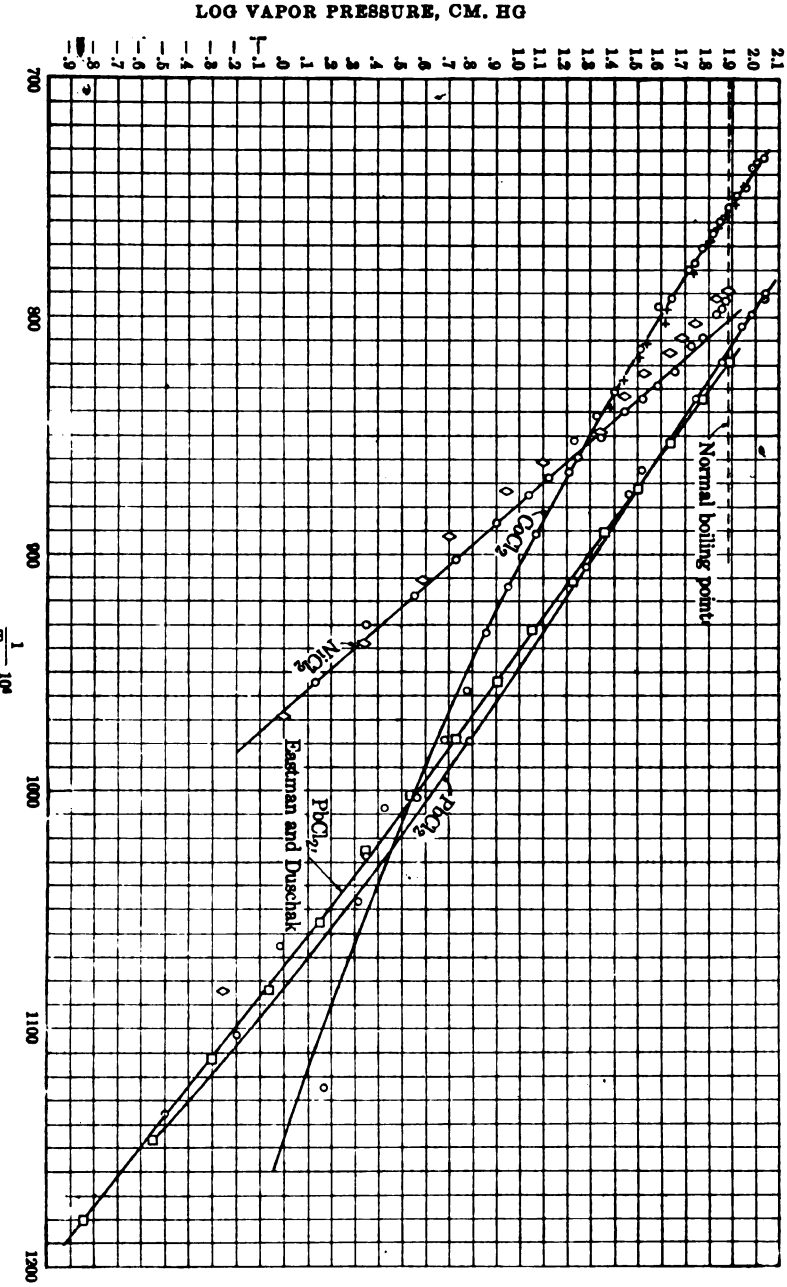

FIGURE 8.—Logarithmic plot of vapor pressures of chlorides of lead, nickel, and cobalt: □, Eastman and Duschak; O, author's values (rising temperatures); +, falling temperatures ($CoCl_2$); ◇, duplicate $NiCl_2$, different preparation of sample

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TABLE 12.—*Data on vapor pressures of manganous chloride ($MnCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T_{abs}}10^4$
1 to 5	23.7 to 461.6			(K.10^3=8.70±0.04)			
6	798.6	1,071.7	10.33	9.33	1.00	0.00	933.3
7	840.4	1,113.5	12.19	9.68	2.51	.3995	898.0
8	872.5	1,145.6	13.26	9.96	3.30	.5184	873.3
9	887.2	1,160.3	14.21	10.10	4.11	.6138	851.8
10	884.0	1,157.1	14.80	10.08	4.72	.6738	854.2
11	917.5	1,190.6	15.79	10.36	5.43	.7347	839.8
12	942.2	1,215.3	18.95	10.58	8.37	.9224	822.7
13	959.1	1,232.2	21.06	10.72	10.24	1.0102	811.5
14	973.0	1,246.1	22.92	10.82	12.10	1.0828	802.3
15	988.3	1,261.4	24.87	10.98	13.89	1.1423	792.8
16	1,005.0	1,278.1	27.91	11.11	16.80	1.2252	782.8
17	1,021.2	1,293.3	31.36	11.26	20.10	1.3030	773.2
18	1,032.8	1,305.9	33.99	11.35	22.64	1.3549	765.7
19	1,047.4	1,320.5	36.61	11.49	25.12	1.4000	757.2
20	1,074.6	1,347.7	44.80	11.71	33.09	1.5194	742.0
21	1,090.1	1,363.2	49.35	11.87	37.48	1.5737	733.5
22	1,099.5	1,372.6	52.94	11.94	41.00	1.6127	728.3
23	1,105.4	1,378.5	54.59	11.98	42.61	1.6294	725.5
24	1,125.5	1,398.6	57.64	12.14	45.50	1.6580	715.2
25	1,139.7	1,412.8	65.21	12.30	52.91	1.7233	708.0
26	1,150.2	1,423.3	68.93	12.38	56.55	1.7520	702.5

MANGANOUS CHLORIDE

Experimental data ..... Table 12.
Logarithmic plot ..... Figure 5.

PREPARATION

Manganous sulphate (c. p.) was boiled with nitric acid and potassium chlorate, and the precipitated manganese dioxide was carefully washed with distilled water until the washings were free from chlorine and sulphate. The dioxide was dissolved in c. p. hydrochloric acid, and evaporated to dryness with excess acid in a fused silica dish. The solid salt was dehydrated by fusing in a stream of anhydrous hydrochloric acid gas, and further heated to incipient vaporization in dry nitrogen.

NOTES ON DETERMINATION

Traces of chlorine were observable during the last part of the run. Whether this was due to thermal dissociation or to the presence of traces of chloride in a higher state of oxidation was not determined. Inasmuch as the material had been previously heated to the vaporization point, the assumption of a slight thermal decomposition at high temperatures seems slightly more probable.

FERROUS CHLORIDE

Experimental data ..... Table 13.
Logarithmic plot ..... Figure 5.

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TABLE 13.—*Data on vapor pressures of ferrous chloride ($FeCl_2$) at various temperatures*

Test No.	Temperature, ° C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^4$
1 to 8	12.2 to 667.4			($K.10^2=2.05\pm0.03$)			
9	699.0	972.1	21.13	19.93	1.20	0.0790	1,028.5
10	729.2	1,002.3	23.52	20.57	2.95	.4697	997.5
11	762.3	1,035.4	24.85	21.22	3.63	.5600	967.3
12	782.0	1,055.1	26.33	21.62	4.71	.6730	947.5
13	807.6	1,080.7	28.93	22.19	5.74	.7590	925.0
14	821.0	1,094.1	30.27	22.42	7.85	.8949	914.2
15	830.7	1,103.8	31.52	22.63	8.89	.9490	906.3
16	844.8	1,117.9	33.68	22.90	10.78	1.0326	894.3
17	859.7	1,132.8	35.90	23.22	12.68	1.1030	882.8
18	870.4	1,143.5	37.99	23.45	14.54	1.1623	872.8
19	883.5	1,156.6	40.99	23.72	17.27	1.2373	864.5
20	894.5	1,167.6	43.47	23.93	19.54	1.2909	856.7
21	908.7	1,181.8	47.27	24.22	23.05	1.3626	846.1
22	922.8	1,195.9	51.28	24.52	26.76	1.4273	836.0
23	932.1	1,205.2	54.64	24.71	29.93	1.4761	829.2
24	939.5	1,212.6	58.26	24.88	33.38	1.5233	824.5
25	951.0	1,224.1	62.25	25.11	37.14	1.5700	817.0
26	959.3	1,232.4	65.48	25.28	40.20	1.6041	811.0
27	970.9	1,244.0	71.95	25.51	46.44	1.6670	804.1
28	983.3	1,256.4	76.28	25.75	50.53	1.7034	795.9
29	989.2	1,262.3	80.65	25.93	54.72	1.7380	792.0
30	994.9	1,268.0	85.30	26.00	59.30	1.7730	788.5

PREPARATION

Ferrous chloride (c. p.) was dried and dehydrated in a stream of anhydrous hydrochloric acid gas, and subsequently fused in nitrogen with the addition of several pieces of pure iron wire. The iron served to reduce traces of ferric salt remaining unvolatilized.

NOTES ON DETERMINATION

No chlorine was evolved during the run, indicating that no thermal dissociation was taking place and that ferric salt was absent. (See Ferric chloride and pages 52 to 54.)

NICKEL CHLORIDE

Experimental data ..... Tables 14 and 15.
Logarithmic plot ..... Figure 7.

PREPARATION

Two samples were prepared. The first (Table 14), the ordinary c. p. nickel chloride presumably free from iron, was dehydrated by heating in hydrochloric acid gas and nitrogen as usual.

The second sample (Table 15) was dehydrated and freed from iron by heating in a slow stream of dry chlorine at 600° to 700° C. The sample was further reheated to incipient vaporization in a stream of nitrogen. During this last heating some small strips of nickel foil, electrolytically refined from a nickel crucible, were added.

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NOTES ON DETERMINATION

In the determination of the first sample mercury in the trap was fouled at temperatures below the vaporization point of the nickel chloride. The action seemed to be due to traces of ferric chloride, which was noticeably condensed in the capillary.

In the second run no fouling occurred, which indicated that the material had been successfully freed from iron, and that no thermal dissociation was taking place. Although the results on both samples are given and plotted, it is thought, in view of the above, that the results of Table 15 are the more accurate. The difference at the boiling point between the two determinations is seen to be small.

TABLE 14.—*Data on vapor pressures of first sample of nickel chloride ($NiCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs
1 to 4	420.4		(K. 10^3=4.54±0.04)				
5	541.0	814.1	3.89	3.65	0.34	−0.469	1,228.0
6	650.0	923.1	4.65	4.10	.55	−.259	1,084.0
7	759.7	1,032.8	5.59	4.58	1.01	.004	968.8
8	793.3	1,066.4	6.71	4.73	2.18	.339	937.8
9	826.5	1,099.6	8.79	4.88	3.91	.592	910.2
10	848.7	1,121.8	10.04	4.98	5.06	.705	891.3
11	872.1	1,145.2	13.96	5.09	8.87	.948	873.0
12	888.5	1,161.6	17.86	5.16	12.70	1.104	860.3
13	901.6	1,174.7	22.28	5.21	17.07	1.232	851.7
14	906.1	1,179.2	27.17	5.23	21.94	1.341	848.2
15	927.5	1,200.6	33.81	5.35	28.46	1.455	833.0
16	942.9	1,216.0	39.59	5.40	34.19	1.534	822.2
17	954.2	1,227.3	48.16	5.44	42.72	1.631	814.5
18	964.1	1,237.2	55.20	5.49	49.71	1.696	808.3
19	972.7	1,245.8	61.73	5.53	56.20	1.749	802.6
20	977.9	1,251.0	68.98	5.56	63.42	1.802	799.2
21	983.9	1,262.4	76.12	5.61	70.51	1.848	792.0
22	994.0	1,267.1	82.06	5.63	76.43	1.883	789.0

TABLE 15.—*Data on vapor pressures of second sample of nickel chloride ($NiCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs
1 to 10	731.3		(K. 10^3=8.63±0.10)				
11	773.9	1,047.0	10.40	9.04	1.36	0.134	955.0
12	801.8	1,074.9	11.60	9.28	2.32	.366	930.7
13	817.5	1,090.6	13.03	9.43	3.60	.556	916.8
14	835.5	1,108.6	15.01	9.56	5.45	.737	902.3
15	855.0	1,128.0	17.83	9.73	8.10	.908	886.7
16	869.7	1,142.8	20.91	9.88	11.03	1.043	874.7
17	879.5	1,152.6	23.44	9.96	13.48	1.129	867.5
18	891.7	1,164.8	27.71	10.04	17.67	1.247	858.8
19	903.2	1,176.3	32.38	10.13	22.25	1.347	850.0
20	917.6	1,190.7	38.71	10.29	28.42	1.454	839.8
21	925.9	1,199.0	43.90	10.33	33.57	1.525	834.0
22	934.2	1,207.3	50.03	10.41	39.62	1.598	828.3
23	943.7	1,216.8	57.23	10.49	46.74	1.669	822.0
24	958.1	1,231.2	64.25	10.62	53.63	1.729	812.0
25	963.3	1,236.4	71.45	10.66	60.79	1.784	808.6
26	979.3	1,252.4	77.26	10.81	66.45	1.822	798.2
27	982.8	1,255.9	82.86	10.83	72.02	1.858	796.0
28	987.0	1,260.1	85.22	10.89	74.33	1.871	793.2

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TABLE 16.—*Data on vapor pressures of cobalt chloride ($CoCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs
1 to 12	21.8 to 594.0		(K. 10^3=1.269±0.004)				
13	633.3	906.4	12.14	11.50	0.64	−0.194	1,103.0
14	665.3	938.4	12.86	11.90	.96	−.017	1,065.5
15	699.2	972.3	14.59	12.33	2.26	.354	1,028.5
16	724.1	997.2	16.29	12.64	3.65	.563	1,003.0
17	748.9	1,022.0	17.98	12.98	5.00	.699	978.0
18	771.4	1,044.5	19.27	13.23	6.04	.781	958.0
19	799.1	1,072.2	21.14	13.60	7.54	.877	932.6
20	802.8	1,093.9	23.04	13.89	9.15	.961	914.7
21	850.0	1,123.1	26.04	14.24	11.80	1.072	891.0
22	883.4	1,156.5	31.00	14.65	16.35	1.213	864.7
23	915.7	1,188.8	36.49	15.06	21.43	1.331	841.3
24	931.7	1,204.8	40.42	15.28	25.14	1.400	830.8
25	957.7	1,230.8	48.44	15.61	32.83	1.517	812.5
26	984.0	1,257.1	54.96	15.92	39.04	1.592	795.8
27	991.4	1,264.5	60.41	16.03	44.38	1.647	791.2
28	1,010.4	1,283.5	68.54	16.28	52.26	1.718	779.6
29	1,013.5	1,286.6	71.73	16.30	55.43	1.744	777.3
30	1,024.5	1,297.6	76.48	16.42	60.06	1.779	770.8
31	1,035.1	1,308.2	82.96	16.58	66.38	1.821	764.3
32	1,043.4	1,316.5	88.84	16.69	72.15	1.858	759.7
33	1,051.9	1,325.0	93.62	16.80	76.82	1.885	754.5
34	1,062.4	1,335.5	101.07	16.92	84.15	1.925	748.8
35	1,069.1	1,342.2	110.05	17.02	93.03	1.969	745.1
36	1,082.1	1,355.2	115.17	17.19	97.98	1.991	737.7
37	1,087.6	1,360.7	121.10	17.28	103.82	2.016	735.0
38	1,091.6	1,364.7	125.67	17.30	108.37	2.036	733.1
39	1,091.2	1,364.3	125.91	17.30	108.61	2.036	733.2
40	1,086.2	1,359.3	121.98	17.21	104.77	2.020	736.0
41	1,081.1	1,354.2	117.82	17.18	100.64	2.003	738.8
42	1,070.4	1,343.5	111.23	17.03	94.20	1.974	744.4
43	1,068.6	1,341.7	107.69	17.02	90.67	1.957	745.7
44	1,063.1	1,336.2	102.12	16.93	85.19	1.930	748.1
45	1,055.3	1,328.4	97.02	16.81	80.21	1.904	753.0
46	1,047.7	1,320.8	90.99	16.76	74.23	1.871	757.1
47	1,040.1	1,313.2	86.82	16.67	70.15	1.846	761.3
48	1,036.9	1,310.0	83.85	16.61	67.24	1.827	763.3
49	1,030.9	1,304.0	81.08	16.53	64.55	1.810	767.2
50	1,022.3	1,295.4	75.49	16.41	59.08	1.771	771.8
51	1,007.5	1,280.6	70.46	16.38	54.08	1.733	780.8
52	973.8	1,246.9	57.12	15.79	41.33	1.616	802.2
53	952.1	1,225.2	48.27	15.52	32.75	1.515	816.1
54	929.1	1,202.2	43.59	15.23	28.36	1.452	832.0
55	920.1	1,193.2	39.64	15.12	24.52	1.389	838.2
56	937.7	1,210.8	43.06	15.36	27.70	1.443	826.0
57	961.8	1,234.9	49.94	15.66	34.28	1.535	810.5
58	983.3	1,256.4	57.81	15.92	41.89	1.621	795.8

COBALT CHLORIDE

Experimental data ..... Table 16.
Logarithmic plot ..... Figure 7.

PREPARATION

Cobalt acetate (c. p.), the only available salt presumably free from nickel, was used with no analysis other than the makers' label. It was taken down to heavy fumes with concentrated sulphuric acid and diluted with distilled water. Barium chloride was added to the exact end point, the barium sulphate filtered off, and the solution evaporated to dryness with excess hydrochloric acid. Further dehydration with dry hydrochloric acid gas and nitrogen was done in the usual way.

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NOTES ON DETERMINATION

As a check on the extent to which saturation of the vapor phase occurs in the apparatus used in these experiments after the maximum temperature is reached, some readings were taken on a descending temperature scale. The agreement is seen to be almost exact with the results of the ascending scale.

Traces of chlorine were observed at the upper ranges, but whether this was due to thermal dissociation or to the presence of small amounts of impurities was not determined.

CUPRIC CHLORIDE

Experimental data..... Table 17 and pages 52 to 54.
Logarithmic plot..... Figure 9.

TABLE 17.—*Data on vapor pressures of cupric chloride ($CuCl_2$) at various temperatures*

Test No.	Temperature, °C.	Temperature abstracts	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Dissociation and vapor pressures, cm. Hg.	Log_{10}V.P.	$\frac{1}{T}10^5$ abs
1 to 8	25.0 to 290.9		(K_{10^2}=5.497±0.014)				
9	309.7	582.8	32.34	32.04	0.30	−0.523	1,717.0
10	325.2	598.3	33.36	32.90	.46	−.337	1,670.5
11	354.5	627.6	35.32	34.48	.84	−.076	1,594.5
12	382.5	655.6	37.38	36.01	1.37	.137	1,525.5
13	401.4	674.5	39.11	37.09	2.02	.305	1,482.5
14	426.3	699.4	41.95	38.42	3.53	.548	1,430.5
15	436.5	709.6	45.48	38.99	6.49	.812	1,410.0
16	459.8	732.9	49.29	40.29	9.00	.954	1,365.0
17	475.9	749.0	56.25	41.17	15.08	1.178	1,335.5
18	485.1	758.2	62.69	41.70	20.99	1.322	1,319.0
19	491.0	764.1	69.88	42.01	27.87	1.445	1,309.0
20	499.3	772.4	76.74	42.47	34.27	1.535	1,294.5
21	510.2	783.3	91.45	43.06	48.39	1.684	1,276.0
22	511.9	785.0	100.25	43.13	57.12	1.757	1,274.0
23	516.7	789.8	111.93	43.40	68.53	1.836	1,266.5
24	521.0	794.1	122.58	43.67	78.91	1.897	1,259.5
25	523.6	796.7	128.70	43.80	84.90	1.928	1,255.0

PREPARATION

Dehydration of cupric chloride is difficult, inasmuch as thermal dissociation sets in at relatively low temperatures, chlorine being evolved and cuprous chloride remaining. For example, cupric chloride dehydrated and fused at a maximum temperature of 550° C. in a stream of pure dry chlorine at 1 atmosphere pressure gave a residue of almost pure cuprous chloride, with only a trace of cupric salt.

Best results were obtained by drying and dehydrating c. p. cupric chloride in a stream of dry hydrochloric acid gas at carefully controlled temperatures, not less than 150° and not higher than 180°.[7] Continued heating at this temperature is necessary, 10 or 12 hours at a minimum. The brown crystals of anhydrous cupric chloride (apparently pseudomorphic with the hydrated salt) were always pre-

[7] Sabatier, Paul, Sur les chlorures métalliques hydratés: Bull. Soc. Chim., ser. 3, t. 13, June 5, 1895, pp. 598–601.

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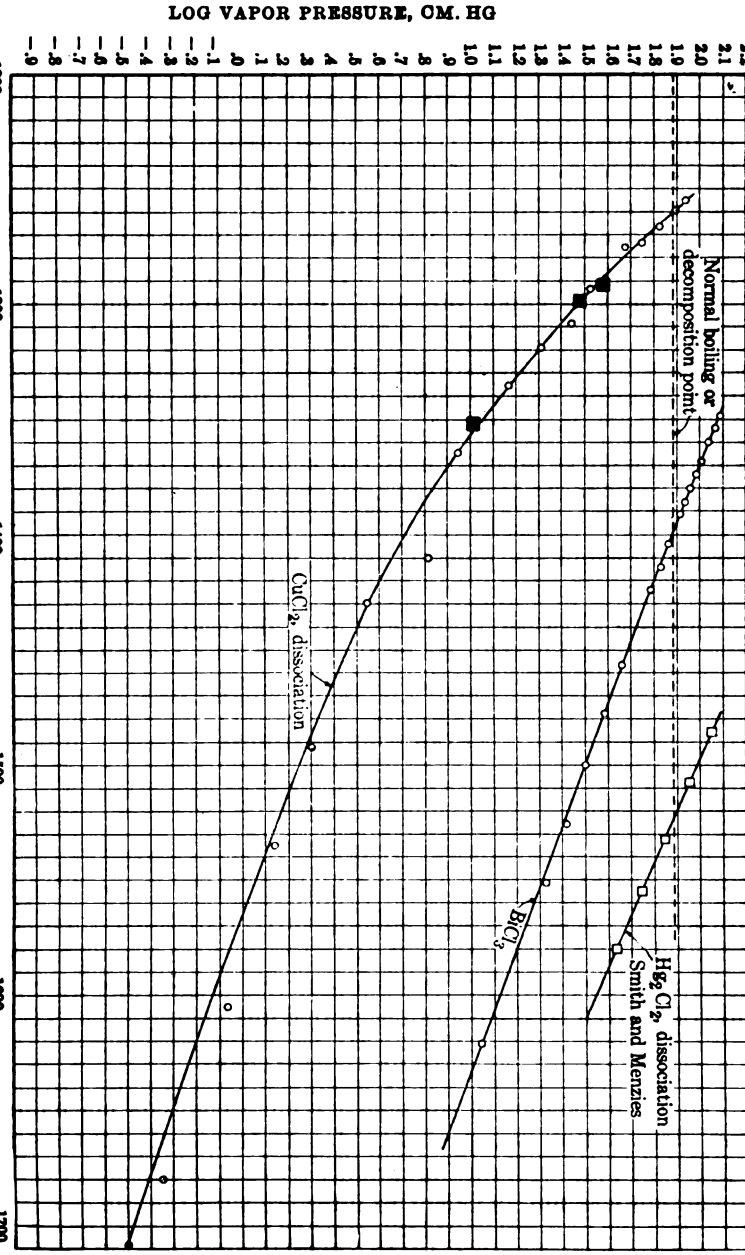

FIGURE 9.—Logarithmic plots of vapor pressure of bismuth, mercurous, and cupric chlorides: ■, by analysis of vapor; O author's values

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pared in the container itself. The material is extremely hygroscopic; it will absorb moisture even in a desiccator containing fresh calcium chloride. It can not be transferred by fusion because of resulting decomposition. It was finally dehydrated in a stream of dry nitrogen at the same temperature.

NOTES ON DETERMINATION

Unprotected mercury could not be used in the trap during this determination, because of the high chlorine concentration developed in the container during the heating. Special sulphuric acid as described above was used to protect the mercury meniscus. The data of Table 17 and the logarithmic plot show presumably the *sum* of dissociation and vapor pressure. Further work (pp. 52 to 54), as far as the accuracy of determination permitted conclusion, showed the vapor to consist entirely of chlorine. Apparently, therefore, cupric chloride has no measurable vapor pressure below its decomposition point. Whether the curvature at the lower end of the logarithmic curve actually exists as shown or is due to experimental error may be doubted. The accuracy when a sulphuric acid protective layer is used over the mercury in the trap is less, due to uncertain changes in capillary depression and slight attack of the mercury. At the upper end the curve approaches a straight line, and the concordance between the values from pressure measurements and those obtained by analysis of the vapor (see pp. 52 to 54) would seem to justify more faith in the accuracy in this range.

STANNOUS CHLORIDE

Experimental data ..... Table 18.
Logarithmic plot ..... Figure 10.

PREPARATION

Stannous chloride (c. p.) was dehydrated in a stream of anhydrous hydrochloric acid gas, and subsequently redistilled three times in pyrex tubes in a slow stream of nitrogen. There was no residue after the last distillation. The final sample was caught in a sealed capsule and transferred to the container in dry nitrogen.

NOTES ON DETERMINATION

A slight blackening of the mercury meniscus took place during the run. This action was probably due to traces of stannous chloride vapor itself, for chlorine invariably gave a white or gray coating. The action was not sufficient to interfere with the run.

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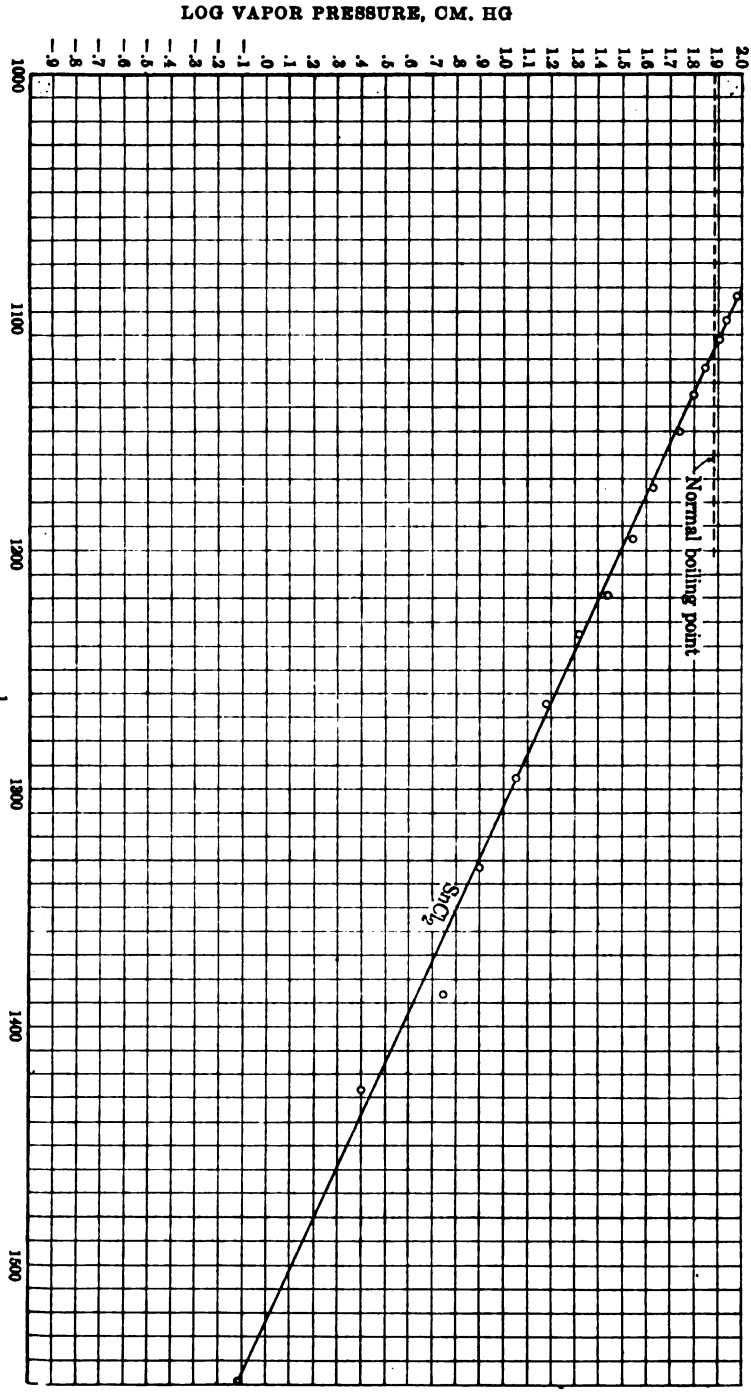

FIGURE 10.—Logarithmic plot of vapor pressures of stannous chloride

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TABLE 18.—*Data on vapor pressures of stannous chloride ($SnCl_2$) at various temperatures*

Test No.	Temperature, ° C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^6$ abs
1 to 3	17.6 to 290.8			($K \cdot 10^3 = 1.993 \pm 0.017$)			
4	372.7	645.8	13.89	12.87	1.02	0.009	1,549.5
5	427.1	700.2	16.47	13.97	2.50	.398	1,428.0
6	447.8	720.9	20.03	14.39	5.64	.751	1,387.0
7	478.0	751.1	23.02	15.00	8.02	.904	1,332.0
8	499.4	772.5	27.06	15.40	11.66	1.067	1,294.5
9	518.0	791.1	31.12	15.78	15.34	1.186	1,264.5
10	536.2	809.3	36.64	16.11	20.53	1.312	1,235.5
11	554.6	827.7	44.05	16.50	27.55	1.439	1,219.0
12	563.1	836.2	51.39	16.70	34.69	1.540	1,195.5
13	579.1	852.2	59.22	17.00	42.22	1.626	1,173.5
14	596.6	869.7	71.07	17.32	53.75	1.730	1,150.0
15	607.5	880.6	79.58	17.58	62.00	1.792	1,135.5
16	617.5	890.6	88.41	17.78	70.63	1.849	1,123.0
17	626.2	899.3	97.70	17.92	79.78	1.902	1,112.0
18	633.9	907.0	106.29	18.09	88.20	1.946	1,103.0
19	641.0	914.1	115.44	18.20	97.24	1.988	1,094.5

GROUP III. TRIVALENT METAL CHLORIDES

The trivalent metal chlorides whose vapor pressures were measured during this work have nearly all appreciable vapor pressures at fairly low temperatures, and a few even at room temperature. Although the oil bath used for these low-boiling materials undoubtedly gave better temperature definition than the tube furnace, the results are probably less satisfactory on the whole than for some of the higher boiling materials. The fact is due not so much to the method being inherently less accurate under these conditions, as to the fact that no refrigeration devices that could be satisfactorily used much below 0° C. were available for this work. Under these circumstances it was not always possible to observe the constancy of K (container constant) over any considerable range, and in many cases K had to be determined by one or two readings at temperatures not very widely separated.

ALUMINUM CHLORIDE

Experimental data ..... Table 19.
Logarithmic plot ..... Figure 11.

PREPARATION

Anhydrous chloride was passed over the best obtainable sheet aluminum at 400° to 500° C. The product was resublimed three times in a vacuum of 2 cm. and preserved in a sealed capsule. It was transferred to the container by sublimation in nitrogen.

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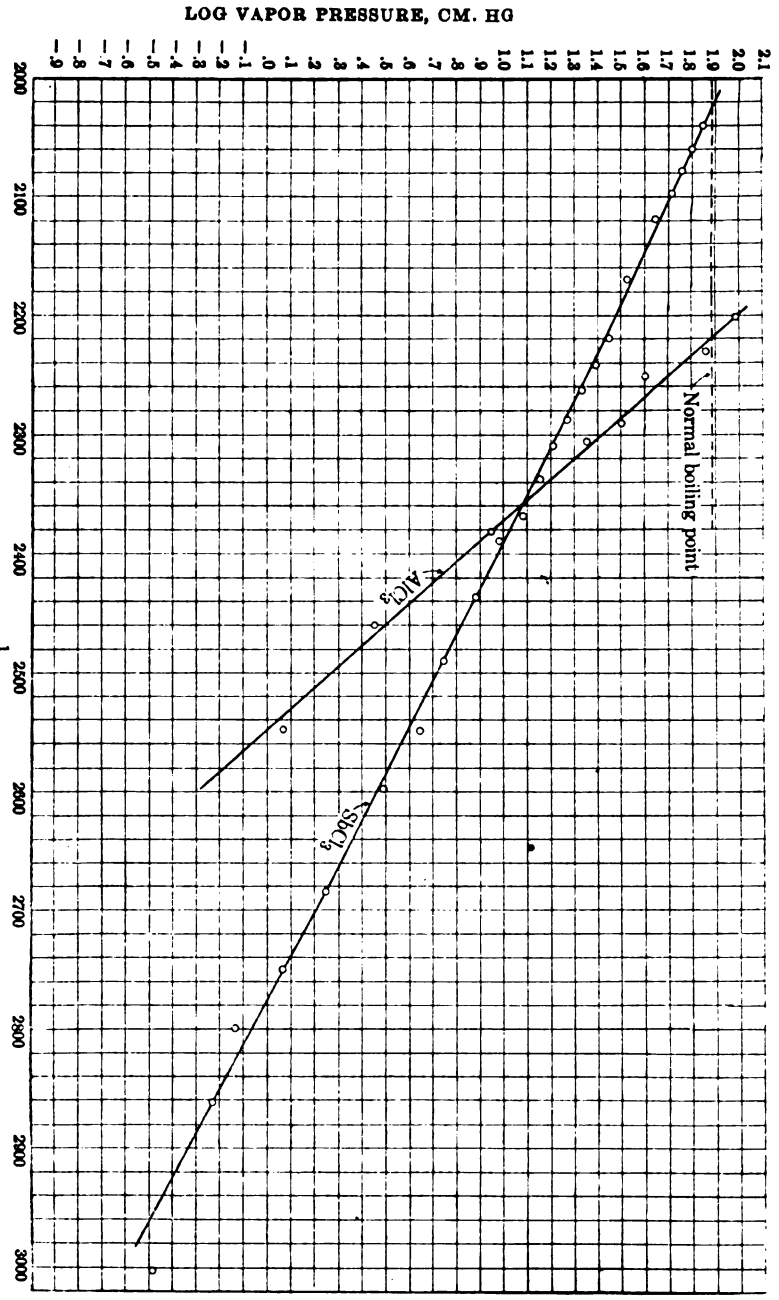

FIGURE 11.—Logarithmic plot of vapor pressures of chlorides of aluminum and antimony

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TABLE 19.—*Data on vapor pressure of aluminum chloride ($AlCl_3$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs
				($K \cdot 10^3 = 4.07$)			
1	21.3						
2	68.8	341.9	1.47	1.39	0.08	−1.097	2.927
3	119.6	392.7	2.79	1.60	1.19	.076	2.548
4	133.0	406.1	5.05	1.65	3.40	.468	2.461
5	146.9	420.0	10.60	1.71	8.89	.948	2.381
6	160.6	433.7	24.59	1.76	22.83	1.359	2.306
7	163.2	436.3	34.14	1.78	32.36	1.509	2.292
8	170.9	444.0	41.96	1.81	40.15	1.603	2.252
9	174.9	448.0	74.18	1.82	72.36	1.859	2.232
10	181.3	454.4	97.86	1.85	96.01	1.983	2.201

NOTES ON DETERMINATION

No fouling of the mercury meniscus of the trap occurred, which indicated that the sample had been freed from chlorine and that thermal decomposition was not taking place.

FERRIC CHLORIDE

Experimental data ..... Table 20.
Logarithmic plot ..... Figure 12.

TABLE 20.—*Data on vapor pressures of ferric chloride ($FeCl_3$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Dissociation and vapor pressures, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs
					($K \cdot 10^3 = 6.21 \pm 0.04$)		
1 to 7	24.1 to 188.8						
8	216.5	489.6	3.43	3.04	0.39	−0.409	2.043
9	237.7	510.8	4.52	3.17	1.35	.130	1.958
10	248.7	521.8	5.90	3.24	2.66	.425	1.916
11	262.5	535.6	8.68	3.32	5.36	.729	1.868
12	273.4	546.5	12.65	3.39	9.26	.967	1.830
13	285.0	558.1	19.71	3.46	16.25	1.211	1.792
14	292.8	565.7	27.71	3.51	24.21	1.384	1.768
15	296.8	569.9	32.68	3.54	29.14	1.464	1.755
16	299.6	572.7	37.65	3.56	34.09	1.533	1.746
17	304.7	577.8	48.77	3.58	45.19	1.655	1.731
18	308.8	581.9	60.03	3.61	56.42	1.751	1.719
19	313.3	586.4	76.60	3.64	72.96	1.863	1.705
20	316.2	589.3	86.73	3.66	83.07	1.919	1.696
21	318.4	591.5	90.93	3.67	87.26	1.941	1.692

PREPARATION

Anhydrous chlorine was passed over pure iron wire (electrolytic) at 400° to 500° C., and the product resublimed three times in chlorine. Sublimation in a vacuum is not possible without some decomposition and formation of the ferrous chloride. The sample was transferred from the sealed capsule to the container in nitrogen. During these sublimations care was taken not to permit the temperature to rise above 300° C.

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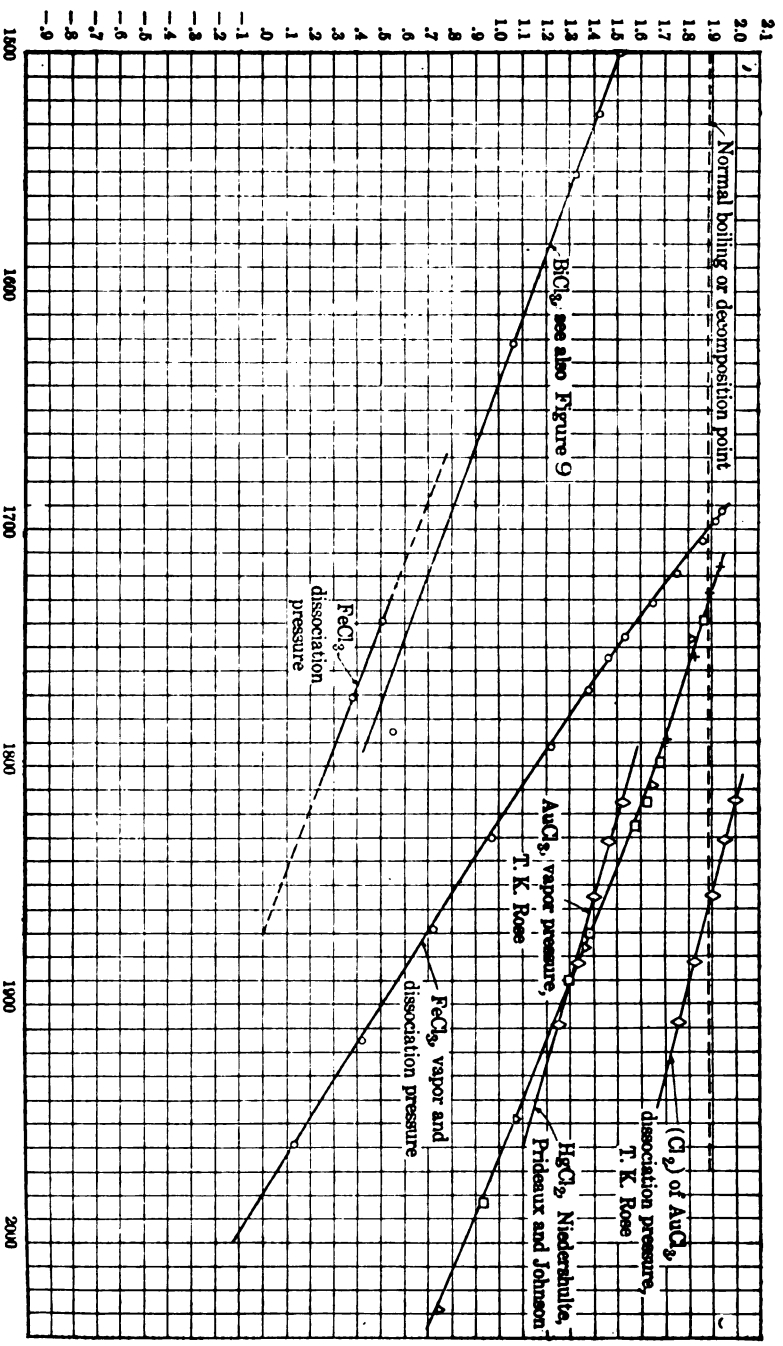

FIGURE 12.—Logarithmic plot of vapor pressures of bismuth, ferric, mercuric, and auric chlorides: □, Johnson; △, Niederhuite; +, Prideaux; ◇, T. K. Rose; ○, author's values

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NOTES ON DETERMINATION

Ferric chloride has a low but definite thermal decomposition pressure below its normal sublimation temperature. A protective layer of sulphuric acid on the mercury in the trap was necessary, as with cupric chloride. Tests of the dissociation pressure are described on pages 52 to 54.

ARSENIC TRICHLORIDE

Experimental data ..... Table 21.
Logarithmic plot ..... Figure 13.

PREPARATION

Resublimed c. p. arsenious oxide was distilled in concentrated sulphuric acid with the addition of c. p. sodium chloride which had been previously fused in platinum. The distillate was fractionated three times, the last time in a slow stream of nitrogen, and preserved in a sealed capsule.

TABLE 21.—*Data on vapor pressures of arsenic trichloride ($AsCl_3$) at various temperatures*

Test No.	Temperature, ° C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	Log$_{10}$ V. P.	$\frac{1}{T}10^4$ abs
				(K=3.3 10^{-4})			
1	8.7	281.8	2.17	0.93	1.24	0.094	3,550
2	27.1	300.2	2.97	.99	1.98	.297	3,332
3	38.2	311.3	5.88	1.03	4.85	.686	3,213
4	49.5	322.6	9.04	1.07	7.97	.901	3,102
5	53.6	326.7	10.39	1.08	9.31	.969	3,063
6	61.1	334.2	14.51	1.10	13.41	1.128	2,992
7	67.0	340.1	16.06	1.12	14.94	1.174	2,941
8	71.0	344.1	18.04	1.14	16.90	1.228	2,907
9	75.5	348.6	21.11	1.15	19.96	1.292	2,870
10	78.8	351.9	23.41	1.16	22.25	1.347	2,844
11	83.4	356.5	27.06	1.18	25.88	1.413	2,806
12	84.3	357.4	28.18	1.18	27.00	1.431	2,798
13	89.1	362.2	31.87	1.20	30.67	1.487	2,762
14	92.0	365.1	34.84	1.21	33.63	1.527	2,739
15	94.1	367.2	36.64	1.21	35.43	1.550	2,723
16	98.0	371.1	41.57	1.22	40.35	1.606	2,696
17	101.1	374.2	45.22	1.23	43.99	1.643	2,673
18	103.4	376.5	48.01	1.24	46.77	1.670	2,657
19	108.3	381.4	53.90	1.26	52.64	1.721	2,623
20	111.4	384.5	58.77	1.27	57.50	1.759	2,602
21	112.1	385.2	60.44	1.27	58.17	1.765	2,597
22	113.2	386.3	62.48	1.27	61.21	1.787	2,590
23	115.2	388.3	66.37	1.28	65.09	1.813	2,578
24	116.8	389.9	68.88	1.28	67.60	1.830	2,568
25	118.2	391.3	70.88	1.29	69.59	1.843	2,558
26	119.4	392.5	72.83	1.30	71.53	1.855	2,549
27	120.4	393.5	73.73	1.30	72.43	1.859	2,543
28	121.0	394.1	74.91	1.30	73.61	1.867	2,538
29	122.0	395.1	77.60	1.30	76.30	1.882	2,531
30	123.0	396.1	77.77	1.31	76.46	1.883	2,526
31	124.0	397.1	79.89	1.31	78.58	1.895	2,519

NOTES ON DETERMINATION

The container shown in Figure 4 was used for this determination. The zero reading is probably inaccurate, because of the impossibility of securing in this work a temperature low enough to make the vapor pressure of the material in the container negligible at the lowest reading of the determination. Temperatures were read from a single-group five-multiple thermocouple, but these readings checked to within 0.2° with a standardized thermometer.

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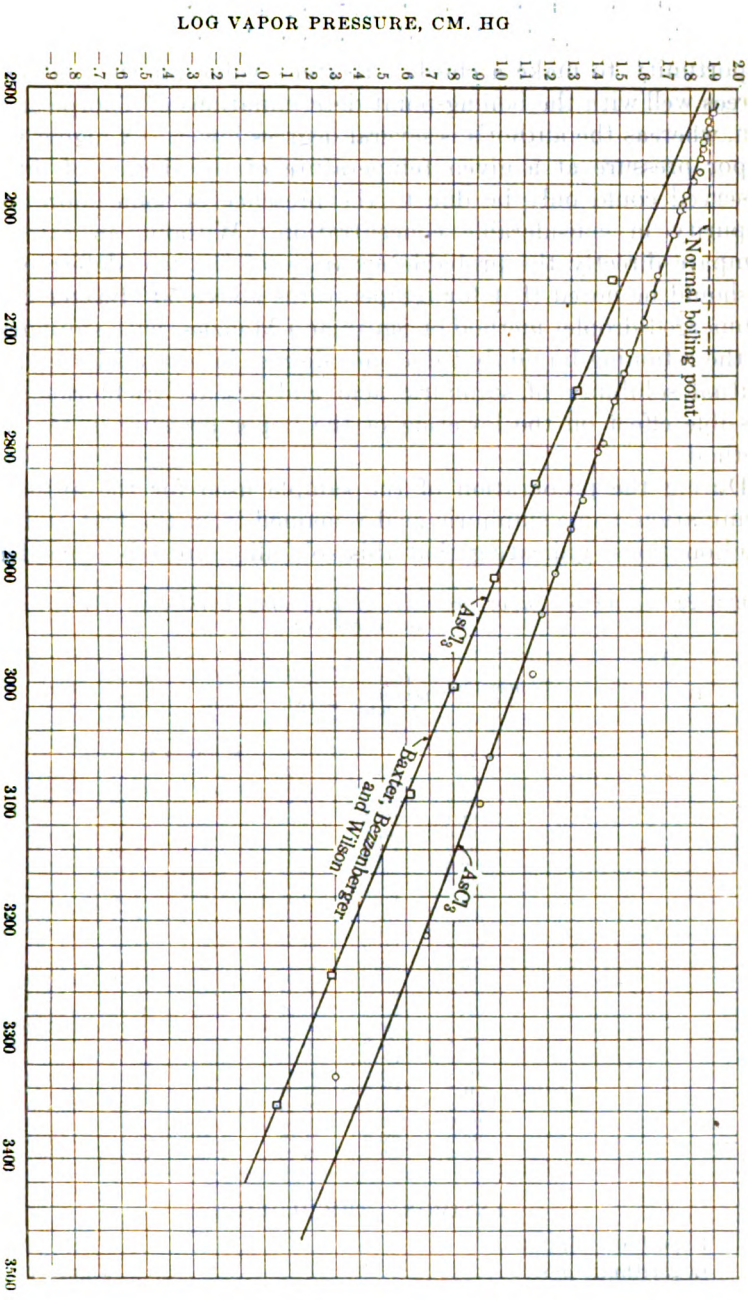

FIGURE 13.—Logarithmic plot of vapor pressures of arsenic trichloride; O, author's values

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The values obtained do not check as well as might be desired with the determinations of Baxter, Bezzenberger, and Wilson[8] on the same material. The determination on arsenic trichloride was the last of those made by the author, and unfortunately there was not opportunity to make a check. Baxter's value for the boiling point agrees well with the boiling-point determinations of Thorpe and Walden, whereas the author's is several degrees lower. A higher value of vapor pressure at a given temperature of the degree of difference observed could only be due to the presence of some more volatile impurity in considerable concentration. Without an attempt to compare directly the probable accuracy of the two determinations, it should be noted that for temperatures above 50° Baxter used the submerged-droplet method of Smith and Menzies, with sulphuric acid as the retaining liquid, but does not discuss in his article the possible mutual solubility of sulphuric acid and arsenic trichloride, nor its possible effect on the lowering of the vapor pressure in the droplet method.

During the preparation of the sample used for the author's determination, some sulphuric acid remained from the first and second fractionations, indicating that this solubility must be considered.

TABLE 22.—*Data on vapor pressures of antimony trichloride ($SbCl_3$) at various temperatures*

Test No.	Temperature, C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1}{T}10^3$ abs
1	27.1			(K. 10^3=3.75)			
2	50.3	323.4	1.26	1.15	0.11	−0.958	3.093
3	59.9	333.0	1.53	1.19	.34	−.468	3.003
4	76.3	349.4	1.84	1.25	.59	−.229	2.862
5	84.4	357.5	2.02	1.27	.75	−.125	2.800
6	90.9	364.0	2.47	1.30	1.17	+.068	2.750
7	99.7	372.8	3.13	1.33	1.80	.255	2.684
8	112.0	385.1	4.50	1.37	3.13	.496	2.598
9	119.4	392.5	5.77	1.40	4.37	.640	2.550
10	128.8	401.9	7.13	1.43	5.70	.756	2.490
11	137.5	410.6	9.21	1.47	7.74	.888	2.437
12	145.3	418.4	11.20	1.49	9.71	.987	2.391
13	149.8	422.9	13.54	1.51	12.03	1.081	2.366
14	155.4	428.5	15.97	1.53	14.44	1.160	2.336
15	160.0	433.1	17.96	1.55	16.41	1.215	2.310
16	164.3	437.4	20.37	1.56	18.81	1.275	2.288
17	168.9	442.0	23.27	1.58	21.89	1.336	2.263
18	173.3	446.4	26.35	1.59	24.76	1.393	2.241
19	177.8	450.9	29.57	1.61	27.96	1.446	2.219
20	187.9	461.0	35.20	1.65	33.55	1.526	2.170
21	199.3	472.4	46.33	1.69	44.64	1.650	2.118
22	204.5	477.6	53.88	1.71	52.17	1.717	2.096
23	208.4	481.5	59.24	1.72	57.52	1.760	2.078
24	212.5	485.6	64.86	1.74	63.12	1.800	2.061
25	216.9	490.0	71.89	1.75	70.14	1.846	2.041
26	226.4	499.5	79.73	1.78	77.95	1.891	2.002

ANTIMONY TRICHLORIDE

Experimental, data ..... Table 22.
Logarithmic plot ..... Figure 11.

[8] Baxter, G. P., Bezzenberger, F. K., and Wilson, C. H., The vapor pressures of certain substances: Chloropicrin, cyanogen bromide, methyl-dichloroarsine, phenyl-dichloroarsine, diphenyl-chloroarsine and arsenic trichloride: Jour. Am. Chem. Soc., vol. 42, July, 1920, pp. 1386-1393.

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PREPARATION

A sample of presumably c. p. antimony trioxide was found to contain small amounts of antimony in a higher state of oxidation. The sample was consequently dissolved in c. p. hydrochloric acid, precipitated with a hot solution of c. p. sodium carbonate in excess, boiled, and the precipitate washed three times with hot distilled water. The precipitate was redissolved in hydrochloric acid and reprecipitated by hydrolysis as oxychloride. The two precipitations were repeated once more, and the final material dehydrated and converted to chloride in a stream of dry hydrochloric acid gas. A final fractionation of the chloride was carried out in a vacuum of 2 cm. and transferred to the container in nitrogen.

NOTES ON DETERMINATION

No unusual behavior was noted. The oil-bath type of apparatus was used.

BISMUTH TRICHLORIDE

Experimental data ..... Table 23.
Logarithmic plots ..... Figures 14 and 17.

PREPARATION

The purest available bismuth compound was c. p. sodium bismuthate. The material was dissolved in concentrated hydrochloric acid and the solution decanted from a slight insoluble residue. Dehydration was carried out in a stream of anhydrous hydrochloric acid gas, after which the material was fractionally distilled in a vacuum of 2 cm. and in a stream of dry nitrogen until no residue appeared on complete volatilization.

TABLE 23.—*Data on vapor pressures of bismuth trichloride ($BiCl_3$) at various temperatures*

Test No.	Temperature, °C.	Temperature, absolute	Pressure observed, cm. Hg	Pressure calculated, cm. Hg	Vapor pressure, cm. Hg	$\log_{10}$ V. P.	$\frac{1\ 10^6}{T_{abs}}$
1 to 3	22.0			(K. 10^3=3.53±0.03)			
4	94.1	367.2	1.98	1.30	0.68	−0.168	2,722
5	122.3	395.4	2.33	1.40	.93	−.032	2,530
6	139.3	412.4	2.45	1.46	.99	−.004	2,426
7	174.0	447.1	2.89	1.58	1.31	+.117	2,237
8	212.3	485.4	3.67	1.71	1.96	.292	2,061
9	240.4	513.5	4.30	1.81	2.49	.396	1,948
10	287.3	560.4	5.60	1.98	3.62	.559	1,785
11	343.7	616.8	13.50	2.18	11.32	1.054	1,621
12	371.4	644.5	23.50	2.28	21.22	1.327	1,551
13	382.3	655.4	28.49	2.31	26.18	1.418	1,526
14	393.3	666.4	34.16	2.36	31.80	1.502	1,500
15	403.2	676.3	40.84	2.39	38.45	1.385	1,478
16	413.8	686.9	47.48	2.42	45.06	1.654	1,456
17	429.2	702.3	63.93	2.48	61.45	1.788	1,424
18	434.0	707.1	70.17	2.50	67.67	1.831	1,414
19	439.0	712.1	75.55	2.52	73.03	1.863	1,404
20	445.1	718.2	83.15	2.53	80.62	1.906	1,392
21	448.7	721.8	88.94	2.55	86.39	1.921	1,386
22	451.3	724.4	93.56	2.56	91.00	1.959	1,380
32	454.9	728.0	99.57	2.57	97.00	1.987	1,373
24	458.5	731.6	104.57	2.58	101.99	2.008	1,368
25	462.3	735.4	109.60	2.60	107.00	2.029	1,360
26	466.1	739.2	118.84	2.61	116.23	2.065	1,353
27	468.8	741.9	123.56	2.62	120.94	2.083	1,349

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TABLE 24.—*Vapor pressures and heats of vaporization of alkali chlorides*

Vapor pressure, atmospheres	Lithium chloride (LiCl)				Sodium chloride (NaCl)			Potassium chloride (KCl)		
	Temperature, °C.[a]	Temperature, °C.[b]	Temperature, °C.[c]	Heat of vapor., cal./mol.	Temperature, °C.[a]	Temperature, °C.[b c]	Heat of vapor., cal./mol.	Temperature, °C.[b]	Temperature, °C.[c]	Heat of vapor., cal./mol.
1.00	[d] 1,353.0	1,385	1,328		[d] 1,411.7	1,442		1,420	1,423	
.75	[d] 1,316.5	1,342	1,293		[d] 1,369.2	1,406		1,376	1,385	
.50	[d] 1,266.4	1,287	1,245	[a] 39,500	[d] 1,313.4	1,358	[a] 38,450	1,322	1,332	[b] 38,490
.25	[d] 1,186.9	1,200	1,170	[b] 40,460	[d] 1,229.	1,282	[b] 45,890	1,235	1,251	[c] 41,330
.10	1,095.4	1,122	1,102	[c] 40,460	1,129	1,102		1,135	1,156	
.05	1,031.7				1,061					
.01	907.2				926					

[a] Author's determination.
[b] von Wartenburg, H., and Albrecht, Ph., Die Dampfdrücke einiger Salze: Ztschr. Electrochemie, Bd. 27, April, 1921, pp. 162–167.
[c] Ruff, Otto, and Mugden, Susanne, Arbeiten aus dem Gebiet hohen Temperaturen XIII. Die Messung von Dampfdrücken bei hohen Temperaturen und die Dampfdrücke der Alkalihalogenide: Ztschr. anorg. Chem., Bd. 117, 1921, pp. 147–171. Ruff, Otto, Schmidt, Gerhard, und Mugden, Susanne, Arbeiten aus dem Gebiet hohen Temperaturen XV. Die Dampfdrücke der Alkalifluoride: Ztschr. anorg. Chem., Bd. 123, 1922, pp. 83–88.
[d] Extropolated values.

NOTES ON DETERMINATION

No unusual behavior was noted during the determination. The tube type of furnace was used.

CALCULATED AND DERIVED RESULTS

TABLES OF VAPOR PRESSURES

Tables 24 to 29, inclusive, contain pressure-temperature values for all the available information concerning chlorides. The data of other investigators, plotted with or without actual determinations by the author, are specially marked on the logarithmic plots. The values of temperatures as contained in these tables were read from the best line representing the data as plotted. Extrapolated values or uncertain values, when recorded, are in brackets.

VALUES OF HEAT OF VAPORIZATION

Tables 24 to 29 also have values for the heats of vaporization as calculated from the plotted values of the logarithmic curves. The usual assumptions are made that the volume of the liquid or solid phase is negligible compared to the volume of vapor, and that the gas laws hold for the vapor. These assumptions are notably not involved in the determination of vapor pressure itself by the present method. From the Clausius equation and the gas law under these assumptions, therefore,

$$-L = R\frac{\partial \operatorname{Ln} p}{\partial\left(\frac{1}{T}\right)},$$

and the values given are those calculated from the slope of the tangent to the logarithmic vapor-pressure curves as plotted in Figures 4 to 13, using 1.988 as the value of R in calories. Results are consequently gram calories per molecule.

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TABLE 25.—*Vapor pressures and heats of vaporization of heavy-metal monovalent chlorides*

Vapor pressure, atmospheres	Cuprous chloride (CuCl)		Silver chloride (AgCl)		Sodium-silver chloride ($NaAgCl_2$)		Mercurous chloride (HgCl)[b]	
	Temperature, °C.[a]	Heat of vapor., cal./mol.	Temperature, °C.[a]	Heat of vapor., cal./mol.	Temperature, °C.	Heat of vapor., cal./mol.	Temperature of dissociation	Heat of reaction[c] cal./mol.
1.00	[d] 1,436.0	16,990	[d] 1,431.4		Unstable		383.2	20,200
.75	[d] 1,342.2	16,990	[d] 1,391.9		do		371.1	
.50	[d] 1,276.4	16,990	[d] 1,341.9		do		355.0	20,200
.25	1,062.3	16,990	1,260.0	42,430	1,295.4	16,510		
.10	896.4	16,990	1,166.2		1,066.1			
.05	815.0	20,640	1,101.7	42,430	928.4			
.01	780.6	23,890	975.9		701.5	16,510		

[a] Author's determination.
[b] Smith, Alexander, and Menzies, A. W. C., Studies in vapor pressure VI. A quantitative study of the constitution of calomel vapor: Jour. Am. Chem. Soc., vol. 32, December, 1910, pp. 1541–1555.
[c] Presumably vaporization+dissociation.
[d] Extrapolated value.

NOTE.—Vapor is Hg+$HgCl_2$.

TABLE 26.—*Vapor pressures and heats of vaporization of divalent chlorides, second periodic group*

Vapor pressure, atmospheres	Zinc chloride ($ZnCl_2$)		Cadmium chloride ($CdCl_2$)		Magnesium chloride ($MgCl_2$)		Barium chloride ($BaCl_2$)		Mercuric chloride ($HgCl_2$)[a]	
	Temperature, °C.[b]	Heat of vapor., cal./mol.	Temperature, °C.[b]	Heat of vapor., cal./mol.	Temperature, °C.[b]	Heat of vapor., cal./mol.	Temperature, °C.[b]	Heat of vapor., cal./mol.	Temperature, °C.	Heat of vapor., cal./mol
1.00	732.4	27,905	969.6	26,440	[c] 1,411.9		1,562		304.1	13,930
.75	713.3	28,100	923.9	27,890	[c] 1,364.0				291.1	15,430
.50	185.4	28,470	898.7	32,110	[c] 1,305.4				275.8	17,200
.25	642.4	29,295	840.0	34,190	1,212.7	35,210			254.0	18,600
.10	594.8	31,870	777.4	35,330	1,108.5				228.9	18,600
.05	563.0	32,060	735.0		1,036.9		1,309	59,900		
.01	500.2	33,210	655.1		896.9	35,210	1,201			
.001							1,066	59,900		

[a] Combined results: Johnson, F. M. G., The vapor pressure of mercuric chloride, bromide, and iodide: Jour. Am. Chem. Soc., vol. 33, June, 1911, pp. 777–781. Prideaux, E. B. R., The vapor pressure and molecular volumes of the mercuric halides and the relations between atomic volumes of elements before and after combination: Jour. Chem. Soc. Trans., vol. 97 1910, pp. 2032–2044; Wiedermann, E., Über Dampfdruke, besonders solche von festen Körpern, nach Untersuchungen von K. Stelzer und G. Niederschulte: Ber. Deut. phys. Gesell., Jahrg. 7, 1905, pp. 159–162.
[b] Author's determinations.
[c] Extrapolated values.

TABLE 27.—*Vapor pressures and heats of vaporization of divalent chlorides, iron group, and manganese*

Vapor pressure, atmospheres	Ferrous chloride ($FeCl_2$)		Nickel chloride ($NiCl_2$)		Cobalt chloride ($CoCl_2$)		Manganese chloride ($MnCl_2$)	
	Temperature, °C.[a]	Heat of vapor., cal./mol.	Temperature, °C.[a]	Heat of vapor., cal./mol.	Temperature, °C.[a]	Heat of vapor., cal./mol.	Temperature, °C.[a]	Heat of vapor., cal./mol.
1.00	1,023.4	32,110	973.4	53,410	1,049.0	30,610	1,190.4	28,780
.75	993.4		957.4		1,017.0	29,700	1,149.0	29,580
.50	954.4		935.2		972.4	28,520	1,096.0	30,610
.25	892.7		897.7		900.2	25,750	1,017.4	32,520
.10	821.1		853.4		805.2	22,410	934.0	36,020
.05	772.1		820.6		730.0	20,190	882.1	38,300
.01	674.4	32,110	752.6	53,410	572.9		785.4	

[a] Author's determination.

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TABLE 28.—*Vapor pressures and heats of vaporization of divalent chlorides, remaining groups*

Vapor pressure, atmospheres	Cupric chloride ($CuCl_2$)		Lead chloride ($PbCl_2$)			Stannous chloride ($SnCl_2$)	
	Dissociation temperature, °C.	Heat of vapor., cal./mol.	Temperature, °C.[a]	Temperature, °C.[b]	Heat of vapor., cal./mol.[a]	Temperature, °C.[a]	Heat of vapor., cal./mol.
1.00	520.6	48,000	954.4	948.4	29,510	622.8	21,130
.75	512.9	45,820	926.7	922.7	29,710	601.2	.....
.50	502.5	43,800	888.0	888.5	29,800	573.0	.....
.25	482.6	38,300	828.4	834.9	30,200	528.6	.....
.10	453.3	30,600	762.7	771.9	32,110	478.7	.....
.05	428.4	26,210	718.9	726.6	34,010	441.7	.....
.01	356.7	.....	637.7	.....	.....	371.4	21,100

[a] Author's determinations.
[b] Eastman, E. D., and Duschak, L. H., **The vapor pressure of lead chloride: Tech. Paper 225,** Bureau of Mines, 1919, 16 pp.

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TABLE 29.—*Vapor pressures and heats of vaporization of trivalent chlorides*

Vapor pressure, atmospheres	Aluminum chloride ($AlCl_3$)		Ferric chloride ($FeCl_3$)[a]		Arsenic trichloride ($AsCl_3$)			Antimony trichloride ($SbCl_3$)		Bismuth trichloride ($BiCl_3$)		Auric chloride ($AuCl_3$)[b]	
	Temperature, °C.[c]	Heat vap. cal./mol.	Temperature, °C.[c]	Heat vap. cal./mol.	Temperature, °C.[c]	Temperature, °C.[d]	Heat vap. cal./mol.	Temperature, °C.[c]	Heat vap. cal./mol.	Temperature, °C.[c]	Heat vap. cal./mol.	Vaporization	Dissociation
1.00	177.8	26,380	315.0	35,470	121.9	128.7	7,630	220.2	10,700	442.2	18,300	.....	265.0
.75	173.6	.....	309.2	35,090	111.0	119.3	7,920	207.5	10,770	426.1	17,530	.....	251.0
.50	167.3	.....	301.4	34,110	96.5	106.8	8,030	190.8	10,830	403.7	17,160	285.0	.....
.25	157.3	.....	288.2	32,480	73.8	87.5	8,110	164.9	11,080	368.8	16,940	253.5	.....
.10	144.9	.....	270.7	30,590	49.2	64.6	8,600	136.9	11,620	326.9	16,410	.....	.....
.05	135.9	.....	256.9	29,410	23.6	48.8	8,900	118.0	12,110	299.7	.....	.....	.....
.01	116.7	26,380	227.1	.....	4.5	27.9	.....	81.2	.....	.....	.....	.....	.....

[a] Vapor plus dissociation pressure, latter low (see pages 52 to 54).
[b] Rose, T. K., The dissociation of chloride of gold: Jour. Chem. Soc. (London), vol. 67, 1895, pp. 881–904.
[c] Author's determinations.
[d] Baxter, G. P., Bezzenberger, F. K., and Wilson, C. H., The vapor pressures of certain substances: Chloropicrin, cyanogen, bromide, methyl-dichloroarsine, phenyl-dichloroarsine, diphenyl-chloroarsine, and arsenic trichloride: Jour. Am. Chem. Soc., vol. 42, July, 1920, pp. 1386–1393. NOTE.—Heat Vap. (3) 9730.

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No attempt has been made to find empirical interpolation formulas for the experimental data, chiefly because of the wide variation of the heat of vaporization of some of the chlorides. The pressure-temperature tables, 24 to 29, reading atmospheres-degrees (Centigrade), cover the ranges of greatest use for engineering purposes.

ACCURACY OF RESULTS

The experimental values of calculated pressures involved in the calculation of vapor pressure deviate from constancy about 0.5 per cent on the average. At low values of vapor pressure this figure probably represents about the range of inaccuracy as far as actual pressure measurements are concerned. At higher pressures, since the calculated pressure is only a small fraction of the total pressure, the uncertainty is thought to be less.

The probable or possible error of temperature measurements is more serious. Table 30 shows the differences between observed boiling points and the average values for other investigators where satisfactory figures were available. The values for this method are both lower and higher, but with an average deviation of $-2.6°$ C. Inasmuch as the temperature range covered is well above 1,400°, the probable inaccuracy of the method is no greater than the possible accuracy of temperature measurement permits. With the apparatus available the *absolute* accuracy of temperature determination at 1,000° is probably not greater than $\pm 5°$ at 1,000°, and correspondingly less at lower temperatures.

The method is obviously unsuited for vapor-pressure determinations where the pressure is less than of the order of magnitude of 1 centimeter of mercury. For anything above this, or for approximate values down to 0.5 mm. the method is thought to be satisfactory for engineering purposes.

TABLE 30.—*Comparison of boiling points*

	Author's determinations	Other values combined	Difference
	°C.	°C.	°C.
1 $ZnCl_2$	732. 4	730. 0	+2. 4
2 $CdCl_2$	969. 6	964	+5. 6
3 $PbCl_2$	954. 4	952. 2	+2. 2
4 $AsCl_3$	121. 9	128. 7	−6. 8
5 $SbCl_3$	220. 2	223	−2. 8
6 $BiCl_3$	442. 2	447	−4. 8
7 $SnCl_2$	622. 8	606	+16. 8
8 $AlCl_3$	177. 8	181. 5	−3. 7
9 $LiCl_3$	1, 353	1, 356. 5	−3. 5
10 NaCl	1, 412	1, 442	−30
Average deviation			−2. 6

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SUMMARY

A method to determine vapor pressures up to 1,250° C. is described. The method is static and direct, and involves no assumptions relative to the behavior of the vapor according to the gas law.

The vapor pressures of the commoner metallic chlorides have been determined over this range.

Available data on the vapor pressures and decomposition pressures of nearly all common metallic chlorides have been assembled in Tables 24 to 29.

Boiling points of the common metallic chlorides are given in Table 31.

Heats of vaporization of the common metallic chlorides as calculated from vapor-pressure data are given in Tables 24 to 29.

TABLE 31.—*Normal boiling points, arranged with decreasing temperatures*

Chloride	Author's determinations	Other determinations
	°C	°C
$CaCl_2$	[1, 600]. 0	
$BaCl_2$	[1, 562]	
CuCl	1, 436	Usually given from 950 to 1,150.
AgCl	1, 431	
KCl	----------	1,420. Von Wartenburg. (See footnote *b*, p. 46.) 1,423. Ruff. (See footnote *c*, p. 46.)
$MgCl_2$	1, 411. 9	
NaCl	1, 411. 7	1,442. Von Wartenburg and Ruff
LiCl	1, 353	1,385. Von Wartenburg. (See footnotes *b* and *c*, p. 46.) 1,328. Ruff.
$MnCl_2$	1, 190. 4	
$CoCl_2$	1, 049	
$NiCl_2$	973. 4	
$CdCl_2$	969. 6	964. Weber, O. H., Über die Änderungen der freien Energie bei geschmolzenen Halogenverbindungen einiger Metalle: Ztschr. anorg. Chem., Bd. 21, 1899, p. 344.
$PbCl_2$	954. 4	948.5. Eastman and Duschak replotted. (See footnote 1, p. 48.) 956. Weber, A. H., Work cited, p. 319.
$ZnCl_2$	732. 4	730. F. Freyer and V. Meyer.—Landolt-Börnstein-Roth. Physikalishe Chemische Tabellen.
$SnCl_2$	622. 8	606. (Bietz, Heinrich, und Meyer, Victor, Über Siedepunkt und Molekulargrösse des Zinnchlorürs, und über gleichzeitige Dampfdichte und Temperaturbestimmungen: Ztschr. phys. Chem., Bd. 2, 1888, pp. 184–193.)
$CuCl_2$ (Dissociation) (Cl_2=1 at.).	520. 6	
$BiCl_3$	442. 2	447. F. Freyer and V. Meyer.—Landolt-Börnstein-Roth. Physikalshe Chemische Tabellen.

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TABLE 31.—*Normal boiling points, arranged with decreasing temperatures*—Con.

Chloride	Author's determinations	Other determinations
	°C	°C
HgCl (Dissociation) ($Hg+HgCl_2=1$ at.).	----------	383.2. Smith, A., and Menzies. (See footnote *b*, p. 47.)
$FeCl_3$	315	
$HgCl_2$	----------	304. Johnson, Prideaux and Wiedemann, combined and replotted. (See footnote *a*, p. 47).
$AuCl_3$ (Dissociation) ($Cl_2=1$ at.).	----------	265. T. K. Rose. (See footnote *b*, p. 49).
$SbCl_3$	220. 2	223. Anshütz and Evans.—Landolt-Börnstein-Roth. Physikalishe Chemische Tabellen.
$AlCl_3$	177. 8	180 to 183. Usually given.
$AsCl_3$	121. 9	128.7. Baxter, Bezzenberger, and Wilson replotted. (See footnote *d*, p. 49.)

DETERMINATION OF DISSOCIATION PRESSURES

In the experiments with cupric or ferric chloride (pages 34 and 40), thermal decomposition to a lower chloride and consequent evolution of chlorine gas takes place. The pressures measured according to the method used for the main part of these experiments are obviously the sum of the vapor and dissociation pressures. To determine the

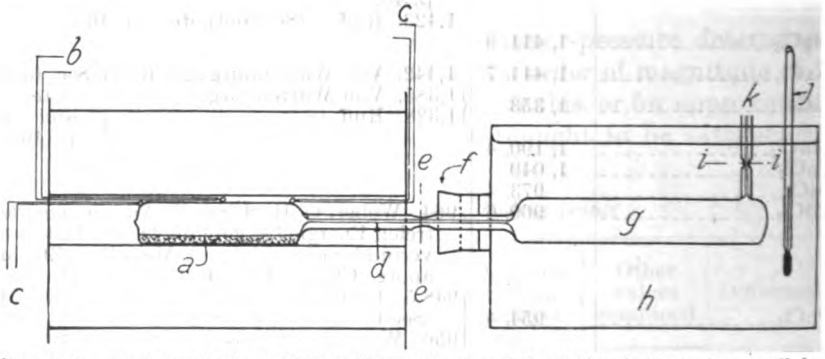

FIGURE 14.—Apparatus for determining equilibrium pressure of dissociable chlorides: *a*, Pyrex cylinder containing chloride; *b*, to cold junction and potentiometer; *c*, to cold junction and millivoltmeter; *d*, capillary outlet; *e-e*, place of seal of equilibrium; *f*, split cork; *g*, empty cylinder; *h*, water bath; *i-i*, place of seal after evacuation before run; *j*, thermometer; *k*, capillary outlet to vacuum pump

relative magnitudes of these two items, experiments of a different sort were necessary.

The apparatus used to determine the relative magnitude of the two pressures is shown in Figure 14. The chloride, ferric or cupric, after dehydration below the decomposition temperature, was placed in a pyrex cylinder, *a*, about 1.8 cm. diameter by 8 cm. long as shown. The capillary outlet, instead of leading to a trap and manometer

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system as before, was directly connected to a similar empty cylinder, *g*, provided with a capillary side tube, *k*, for evacuating and immersed in a water bath, *h*.

After the entire system had been pumped out to about 0.2 mm. pressure, the whole was sealed shut at *i–i*. The cylinder containing the chloride was then heated at a constant temperature for at least 6 hours. The temperature chosen was such that an appreciable dissociation took place, but not enough to produce gas at more than atmospheric pressure. The method is obviously limited to this range, as the pressure must be kept less than atmospheric inside the system so that a seal can be easily made. After equilibrium had been attained (6 hours sufficed under the conditions of the experiments), the two cylinders were sealed off at *e–e*. The empty one, now containing chlorine but no chloride, was removed. This chlorine was now determined by breaking the tip of the capillary seal under a measured volume of standard arsenite solution, and after absorption of the chlorine titrating excess arsenite with standard iodine.

To determine the partial pressure of chlorine the only other data necessary are the total volume of the chlorine container and the temperature of the water bath at the time of seal. Provided equilibrium is attained in the system, the partial pressure of the chlorine in the empty container at the time of seal is equal to the dissociation pressure at the temperature in question. It was found that equilibrium in the reaction $2\ CuCl_2 = Cu_2Cl_2 + Cl_2$ is attained rapidly reading from left to right, but rather more slowly in the reverse direction. Diffusion of the chlorine into the empty cylinder under the low pressure is rapid, but the reverse diffusion is somewhat slow. For this reason care had to be taken in these experiments where the total time available for the system to come to equilibrium was limited, that at no time did the temperature of the chloride cylinder become markedly higher than the constantly regulated temperature at which the run was being made.

The results of the limited number of experiments performed are as follows:

Dissociation pressures

Partial pressure Cl_2 by anal. in cm. Hg	Temperature, °C.	Temperature, absolute.	$\frac{1}{T}10^6$	Log. 10 dissociation pressures
Cupric chloride				
10.44	466.3	739.4	1,353	1.019
29.92	496.3	769.4	1,299	1.476
38.25	501.0	774.1	1,291	1.582
Ferric chloride				
2.41	291.5	564.6	1,771	0.382
3.19	301.8	574.9	1,739	.504

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Comparison of these figures with the logarithmic plots of the total determined pressures of cupric and ferric chlorides, respectively, shows that the chlorine pressure constitutes practically the whole of the measured pressure of the cupric chloride, but only a small part of the total pressure of the ferric salt.

For ferric chloride only two points were determined. The reason for this is that at lower temperatures the chlorine pressure was so low that its analytic determination in the small volumes used in these experiments was difficult, whereas any temperature above those used had so high a vapor pressure that the determination could not be continued long enough to attain equilibrium without vaporizing some of the ferric salt into the chlorine cylinder, or else plugging the capillary.

PUBLICATIONS ON CHLORIDE VOLATILIZATION OF ORES

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BULLETIN 168. Recovery of zinc from low-grade and complex ores, by D. A. Lyon and O. C. Ralston. 1919. 145 pp., 23 figs.

BULLETIN 211. The chlorine volatilization process of ore treatment, by Thomas Varley, E. P. Barrett, C. C. Stevenson, and R. H. Bradford, with an introductory chapter by Stuart Croasdale. 1923. 99 pp., 7 pls., 5 figs.

TECHNICAL PAPER 225. The vapor pressure of lead chloride, by E. D. Eastman and L. H. Duschak. 1919. 16 pp., 2 pls., 2 figs.

TECHNICAL PAPER 317. Silver in chloride volatilization, by C. M. Bouton, W. C. Riddell, and L. H. Duschak. 55 pp., 3 figs.

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BULLETIN 157. Innovations in the metallurgy of lead, by D. A. Lyon and O. C. Ralston. 1918. 176 pp., 13 figs. 20 cents.

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